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MATHEMATICS

On the Asymptotic Behaviour of the Solutions of a System of Ordinary Non-Linear Differential Equations

by

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In the present paper we shall investigate the asymptotic properties of the solutions of a system arising by perturbation of a linear system with constant coefficients of the form

$$\frac{dy_i}{dt}=\sum_{k=1}^{n} a_{ik}\,y_k \qquad (i=1,2,\ldots,n),$$

where y_i are complex numbers and t is real.

1. Notation. System (1) will be written in the vector form

$$\frac{dy}{dt}=Ay, \tag{1}$$

where y denotes an element of the space of n complex variables E, and A denotes a linear operator determined in the given co-ordinate system by the n by n matrix. Let us denote by $\lambda_1,\lambda_2,\ldots,\lambda_m$ the sequence of different characteristic roots of the matrix $\{a_{ik}\}$. Let μ be one of the numbers of that sequence. By $E^{\mathrm{I}},E^{\mathrm{II}},E^{\mathrm{III}}$ we shall denote the subspaces of the space E which are filled by the integrals of system (1), of the form

$$\sum_{\mathrm{Re}\,\lambda_i<\mathrm{Re}\,\mu} e^{\lambda_i t}w_i(t), \qquad e^{\mu t}w(t), \qquad \sum_{\substack{\mathrm{Re}\,\lambda_i\geqslant\mathrm{Re}\,\mu\\ \lambda_i\neq\mu}} e^{\lambda_i t}w^i(t)$$

respectively, where the components of the vector functions $w_i(t)$ and $w(t)$ are polynomials. Denote by β the least integer such that $\|y(t)\|=o(e^{\mathrm{Re}\mu t}t^{\beta})$ *) for every solution $y(t)$ of system (1) contained in E^{II}. Denote by G_i $(i=$

*) $\|y\|=\sqrt{\sum_{i=1}^{n} y_i\bar{y}_i}$, where $y_1,y_2,\ldots,y_n$ are the co-ordinates of vector y and the number $\bar{y}_i$ is conjugate with y_i.

$=1,2,\ldots,\beta)$ the subspaces of the space E^{II} filled by integrals of the form $e^{\mu t}w(t)$, where the components $w(t)$ are polynomials of, at most, the degree $i-1$. In space E^{II} we choose subspaces $E^1,E^2,\ldots,E^\beta$ in such a way that G^i is the simple sum of the spaces $E^1,E^2,\ldots,E^i$ $(i=1,2,\ldots,\beta)$ *). Spaces E^I,E^{II},E^{III} and $G^1,G^2,G^3,\ldots,G^\beta$ (but not spaces $E^2,E^3,\ldots,E^\beta$) are uniquely determined by the operator A. The following equality holds:

$$E=E^I\dot{+}E^{II}\dot{+}E^{III}=E^I\dot{+}E^1\dot{+}E^2\dot{+}\ldots\dot{+}E^\beta\dot{+}E^{III}. \tag{2}$$

In view of (2), an arbitrary vectory belonging to E can be uniquely decomposed into the sum

$$y=y^I+y^{II}+y^{III}=y^I+y^1+y^2+\ldots+y^\beta+y^{III}, \tag{3}$$

where $y^i\in E^i$ $(i=I,II,III,1,2,\ldots,\beta)$.

Making use of decomposition (3) and of the relations

$$Ay^i\in E^i(i=I,II,III);\quad Ay^1-\mu y^1=0;\quad Ay^i-\mu y^i\in G^{i-1} \tag{4}$$
$$(i=2,3,\ldots,\beta)\ **)$$

we can write system (1) in the following form:

$$\frac{dy^I}{dt}=Ay^I;\quad \frac{dy^i}{dt}=\mu y^i+\sum_{j=i+1}^{\beta}A_j^iy^j\quad (i=1,2,\ldots,\beta);\quad \frac{dy^{III}}{dt}=Ay^{III}, \tag{5}$$

where A_j^i denotes the linear operators determined by (3), (4) from the equality $(A-\mu I)y^i=\sum_{i=1}^{i-1}A_j^iy^j$ ***).

Let us consider the space $E_*=E\times(-\infty,+\infty)$. In this space we shall introduce an auxiliary function defined for every $x\in E$ and $t>0$

$$\chi_t(x)=\|x^I\|+\frac{\|x^1\|}{t^{\beta-1}}+\frac{\|x^2\|}{t^{\beta-2}}+\ldots+\|x^\beta\|+\|x^{III}\|\ ****).$$

The function $\chi_t(x)$ is connected with the operator A and the chosen root μ. The following inequality gives a relation between $\chi_t(x)$ and the norm of the vector x:

$$t^{1-\beta}\|x\|\leqslant\chi_t(x)\leqslant\|x\|\ *****). \tag{6}$$

*) The vector space E is said to be the simple sum of subspaces $E^1,E^2,\ldots,E^k$ if for every y belonging to E there exists a uniquely determined system of vectors $y^1,y^2,\ldots,y^k$ such that $y^i\in E^i$ and $y=y^1+y^2+\ldots+y^k$; we then write $E=E^1\dot{+}E^2\dot{+}\ldots\dot{+}E^k$.

**) Relations (4) follow from the definition of the subspaces $E^I,E^1,\ldots,E^\beta,E^{III}$ and from the fact that the derivative of an integral of system (1) is also an integral.

***) After the introduction of a co-ordinate system in spaces E^i, certain rectangular matrices will correspond to these operators.

****) For a fixed $t,\chi_t(x)$ is a certain norm of the vector x lying in the hyperplane $t=$ const. of the space E_*.

*****) Where x^i are components of x, $x=x^I+x^1+\ldots+x^\beta+x^{III}$ $x^i\in E_i$ $(i=I,1,2,\ldots,\beta,III)$.

2. THEOREM 1. *Consider the system of non-linear differential equations,*

$$\frac{dx}{dt}=Ax+\varphi(t,x)+\psi(t,x)+F(t,x), \tag{7}$$

where the vector functions $\varphi(t,x)$, $\psi(t,x)$, $F(t,x)$ *are continuous for* $x\in E$ *and* $t\geqslant 0$ *and satisfy the following assumptions:*

a) $\varphi(t,x)$ *is independent of* x^{II},x^{III}; *the set of values of function* $\varphi(t,x)$ *is contained in* E^{I}; *there exists a positive and continuous function* $\sigma(t)$ *such that*

$$\liminf_{t\to+\infty}\sigma(t)\geqslant\beta+1, \tag{8}$$

$$\operatorname{Re}(x^{I},Ax^{I}+\varphi(t,x^{I}))\leqslant(\operatorname{Re}\mu-\sigma(t))\|x^{I}\|^{2};\ *) \tag{9}$$

b) $\psi(t,x)$ *is independent of* x^{I},x^{II}; *the set of values of function* $\psi(t,x)$, *is contained in* E^{III}; *there exists a continuous function* $\varepsilon(t)$ *such that*

$$\int_{B}^{D}\varepsilon(t)\,dt>-c\quad(c>0\ \text{for arbitrary positive } B,D), \tag{10}$$

$$\operatorname{Re}(x^{III},Ax^{III}+\psi(t,x^{III}))\geqslant(\operatorname{Re}\mu+\varepsilon(t))\|x^{III}\|^{2}; \tag{11}$$

c) *there exists a continuous function* $g(t)$ *such that*

$$\int_{0}^{\infty}g(t)\,dt<+\infty, \tag{12}$$

and such that for every x *and* $t>0$ *we have the inequality*

$$\chi_{t}(F(t,x))\leqslant g(t)\,\chi_{t}(x). \tag{13}$$

Let s *be one of the numbers of the sequence* $1,2,\ldots,\beta$ *and let* ξ_{0} *be an arbitrary vector belonging to* E^{s}. *Denote by* $y_{0}(t)$ *an integral of system* (5) *satisfying the initial condition* $y_{0}(0)=\xi$.

Under these assumptions there exists a family R *of solutions of system* (7) *such that if* $x(t)$ *belongs to* R, *then*

$$\chi_{t}(x(t)-y_{0}(t))=o(e^{\operatorname{Re}\mu t}t^{s-\beta}). \tag{14}$$

Moreover, for an arbitrary $\varrho>0$, *there exists a number* $T>0$ *such that for* $t>T$ *the projection of the right emission zone of the set* K_{ϱ} *with respect to system* (5) **), *upon the subspace* $(E^{I}+G^{s-1})\times(-\infty,+\infty)$ *is contained in the projection of the set filled by integrals of the family* R *upon that sub-*

*) By (a,b) we denote the scalar product of the vectors a,b belonging to E, i. e., if $a=(a_1,a_2,\ldots a_n)$ and $b=(b_1,b_2,\ldots,b_n)$ then $(a,b)=\sum_{i=1}^{n}a_ib_i$.

**) i. e., the set of points $(t,y)(t\geqslant 0)$ lying on the integrals $y(t)$ for which $y(0)\in K\varrho$.

space, K_ϱ denoting the set

$t=0;\ \|y^{\mathrm{I}}\|\leqslant\varrho;\ \|y^{i}\|\leqslant\varrho\ (i=1,2,\dots,s-1);\ y^{s}=\xi_0;\ y^{i}=0\ (i=s+1,\dots,\beta,\mathrm{III}).$

Proof of Theorem 1. By assumptions a) and b) system (7) can be written in the following form:

$$(7')\qquad \begin{cases} \dfrac{dx^{\mathrm{I}}}{dt}=Ax^{\mathrm{I}}+\varphi(t,x)+F^{\mathrm{I}}(t,x), \\ \dfrac{dx^{i}}{dt}=\mu x^{i}+\sum\limits_{j=i+1}^{\beta}A_j^i x^j+F^{i}(t,x)\ (i=1,2,\dots,\beta), \\ \dfrac{dx^{\mathrm{III}}}{dt}=Ax^{\mathrm{III}}+\psi(t,x^{\mathrm{III}})+F^{\mathrm{III}}(t,x). \end{cases}$$

Without reducing the generality of our considerations we can assume that $\mu=0$ *), and also that through every point of space E_* passes exactly one integral of system (7) **).

Using the functions

$$(15)\qquad \begin{aligned} m^{i}(t,x)&=\|x^{i}-y_0^{i}(t)\|-h^{i}(t)\quad (i=\mathrm{I},1,2,\dots,s-1), \\ l^{i}(t,x)&=\|x^{i}-y_0^{i}(t)\|-h^{i}(t)\quad (i=s,\dots,\beta,\ \mathrm{III}), \end{aligned}$$

we shall define the sets $\omega, M^{\mathrm{I}}, M^{1}, M^{2},\dots,M^{s-1},L^{s},\dots,L^{\beta},L^{\mathrm{III}}$, namely:

$\omega:\{t>T;\ m^{i}(t,x)<0\,(i=\mathrm{I},1,\dots,s-1);\quad l^{i}(t,x)<0\quad (i=s,\dots,\beta,\ \mathrm{III})\},$

$M^{i}\{t\geqslant T;\ m^{i}(t,x)=0;\ m^{j}(t,x)\leqslant 0\,(j=\mathrm{I},1,\dots,s-1);\ l^{j}(t,x)\leqslant 0\ (j=s,\dots,\beta,\mathrm{III})\},$

$L^{i}\{t\geqslant T;\ m^{j}(t,x)\leqslant 0\,(j=\mathrm{I},1,\dots,s-1);\ l^{i}(t,x)=0;\ l^{j}(t,x)\leqslant 0\quad (j=s,\dots,\beta,\mathrm{III})\}.$

Functions $h^{i}(t)$ are defined as follows:

$$(16)\qquad h^{\mathrm{I}}(t)=e^{-\int_0^t\sigma(\tau)d\tau}\Big(\varrho+\int_0^t e^{\int_0^\tau\sigma(v)dv}\,Dg(\tau)\tau^{s-\beta}d\tau\Big),$$

$$(17)\qquad h^{i}(t)=\int_t^\infty\Big(C\sum_{j=i+1}^{\beta}h^{j}(\tau)+Dg(\tau)\tau^{s-i}\Big)d\tau\quad (i=s,s+1,\dots,\beta),$$

$$(18)\qquad h^{i}(t)=\varrho+\int_0^t\Big(C\sum_{j=i+1}^{\beta}h^{j}(\tau)+Dg(\tau)\tau^{s-i}\Big)d\tau\quad (i=1,\dots,s-1),$$

$$(19)\qquad h^{\mathrm{III}}(t)=\int_t^\infty e^{-\int_t^\tau\varepsilon(v)dv}\,Dg(\tau)\tau^{s-\beta}d\tau.$$

*) In the contrary case a change of variables $x=e^{-\mu t}u$ leads to a system satisfying all the assumptions of Theorem 1 for $\mu=0$.

**) In view of a remark of T. Ważewski (see [3], p. 313) the result obtained here under the assumption of uniqueness can be transferred to a system which does not satisfy that assumption.

The constants C and D occurring in formulas (16)–(19) are chosen so that $\|A_j^i x^j\| \leqslant \frac{C}{\beta+1}\|x^j\|$ for every i,j and $\chi_t(y_0(t)) < \frac{1}{2} Dt^{s-\beta}$. It follows from the definition of functions $h^i(t)$ and from assumptions (8), (10) and (12) that

$$(20) \qquad \begin{gathered} h^i(t) > 0 \ \ (i = \mathrm{I}, 1, \ldots, \beta, \mathrm{III}); \qquad h^i(t) = o(t^{s-\beta}) \ \ (i = \mathrm{I}, \mathrm{III}); \\ h^i(t) = o(t^{s-i}) \ \ (i = 1, 2, \ldots, \beta). \end{gathered}$$

From (20) and from the definition of the set ω and the constant D, follows the inequality

$$(21) \qquad \chi_t(x) < Dt^{s-\beta} \quad \text{for} \quad (t,x) \in \omega,$$

provided the T occurring in the definition of the set ω is taken sufficiently large. By assumptions (9), (11), (13), relations (16)–(19) and the form of system (7′), it can be proved that for $t \geqslant T$ the following inequalities are valid:

$$(22) \qquad \begin{aligned} &\frac{d}{dt} m^i(t, x(t)) < 0 \quad (i = \mathrm{I}, 1, \ldots, s-1) \quad \text{for every} \quad (t_0, x_0) \in M^i, \\ &\frac{d}{dt} l^i(t, x(t)) > 0 \quad (i = s, \ldots, \beta, \mathrm{III}) \quad \text{for every} \quad (t, x_0) \in L^i, \end{aligned}$$

where $x(t)$ denotes an integral of system (7′) satisfying the initial condition $x(t_0) = x_0$. Denoting by $S = \sum L^i - \sum M^i$, and by $Z_P (P = (t,x))$ the set determined by the relations

$$\begin{gathered} m^i(t,x) = m^i(P) = \text{const.} < 0 \quad (i = \mathrm{I}, 1, \ldots, s-1), \\ l^i(t,x) \leqslant 0 \quad (i = s, \ldots, \beta, \mathrm{III}); \quad t = T, \end{gathered}$$

we can prove that for every P we have the following properties:

$Z_p \subset \omega + S$, $Z_P S$ is a retract of S and $Z_P S$ is not a retract of Z_P.

From this and inequality (22), and from T. Ważewski's theorems (see [3], p. 303, théorème 2, and p. 310, théorème 5), we infer that for every P there exists a Q belonging to Z_P for which the corresponding integral of system (7) always remains in ω for $T \leqslant t < +\infty$. The set of all integrals of system (7′) which remains in ω starting from a certain t, will be denoted by R_ϱ. The family R will be obtained by summing the sets R_ϱ for all possible ϱ. The first part of Theorem 1 follows from (15) and (20), and the second part follows from the fact that the emission zone of the set K_ϱ with respect to system (5) is contained in ω for $t > T$ and that the projection of the set filled by the integrals of family R upon the subspace $(E^{\mathrm{I}} + G^{s-1}) \times (-\infty, +\infty)$ covers the projection of the set ω upon that subspace.

3. Remarks and certain modifications of Theorem 1.

REMARK 1. Function $\chi_t(x)$ depends, as we know, upon the choice of the spaces $E^2,\dots,E^\beta$, but if we denote by χ_t^* an analogous function when these spaces are chosen differently, then there exist constants C_1, C_2, such that $C\,\chi_t(x)\leqslant\chi_t^*(x)\leqslant C_2\chi_t(x)$.

On account of this inequality the assumptions of Theorem 1 are independent of the choice of the spaces $E^2,\dots,E^\beta$.

REMARK 2. The assumption

$$\|F(t,x)\|\leqslant h(t)\|x\|, \quad \text{where} \quad \int_0^\infty t^{\beta-1}h(t)\,dt<+\infty,$$

is stronger than (12) and (13). It follows that the result of Z. Szmydt (see [2], p. 262) can be obtained as a corollary to Theorem 1.

THEOREM 2. *We accept the assumptions of Theorem 1. Moreover, we assume that*

$$\int_0^\infty t^\alpha g(t)\,dt<+\infty, \quad \textit{where } \alpha \textit{ is a positive integer.} \tag{23}$$

Let ξ_0 be an arbitrary vector of spaces $E^{s-\alpha}+E^{s-\alpha+1}+\dots E^s$ if $s-\alpha\geqslant 1$ or spaces $E^1+E^2+\dots+E^s$ if $s-\alpha<1$. Denote by $y_0(t)$ an integral of system (5) satisfying the initial condition $y_0(0)=\xi_0$.

There exists a family R of solutions of system (7) such that if $x(t)$ belongs to R, then

$$\chi_t(x(t)-y_0(t))=o(e^{\mathrm{Re}\mu t}t^{s-\alpha-\beta}), \tag{24}$$

and for every $\varrho>0$ there exists a $T>0$ such that the projection of the right emission zone of the set $K\varrho$ with respect to system (5) upon the subspace $(E^{\mathrm{I}}+G^{s-\alpha-1})\times(-\infty,+\infty)$ if $s-\alpha>1$, or upon the subspace $E^{\mathrm{I}}\times(-\infty,+\infty)$ if $s-\alpha\leqslant 1$, is contained for $t\geqslant T$, in the projection of the set filled by the integrals of family R upon that subspace, $K\varrho$ denoting the set

$$t=0; \quad \|y^i\|\leqslant\varrho\,(i=\mathrm{I},1,\dots,s-\alpha-1);\ y^{s-\alpha}+y^{s-\alpha+1}+\dots+y^s=\xi_0,$$
$$y^i=\theta=(0,0,\dots,0) \quad (i=s+1,\dots,\beta,\mathrm{III}).$$

The proof of this theorem is analogous to the proof of Theorem 1. The following modification of Theorem 1 without any essential changes in the proof will be obtained if we introduce, after P. Hartman and A. Wintner, an auxiliary function $\Phi(t,z)$.

THEOREM 3. *Let us accept the assumptions* a) *and* b) *of Theorem* 1. *Suppose that a continuous and positive function $\Phi(t,z)$ satisfies, for $t>0$ and $z>0$, the following conditions*:

$$\Phi(t,z) \textit{ is non-decreasing with respect to } z \textit{ for fixed } t, \tag{25}$$

$$\int_0^\infty e^{-\mathrm{Re}\mu t}t^{\alpha+\beta-s}\Phi(t,\ \text{const.}\ e^{\mathrm{Re}\mu t}t^{s-1})\,dt<+\infty, \tag{26}$$

where const. is any positive constant and suppose that, for $t \geqslant 1$ *and every* x, *we have the inequality*

$$\chi_t(F(t,x)) \leqslant \Phi(t, t^{\beta-1}\chi_t(x)). \tag{27}$$

Under these assumptions Theorem 2 holds.

In view of the inequality

$$\chi_t(x) \leqslant \|x\| \leqslant t^{\beta-1}\chi_t(x) \quad \text{for} \quad t \geqslant 1,$$

Theorem 3 is more general than P. Hartman and A. Wintner's theorem concerning an analogous problem (see [1], p. 709, (+)).

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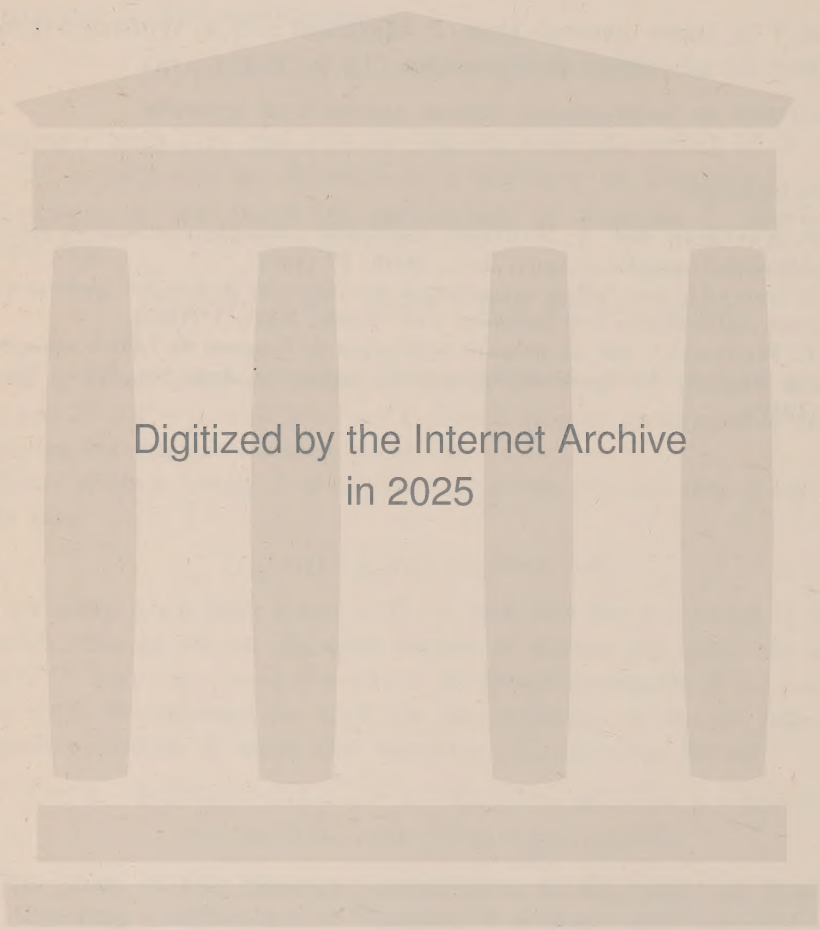
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MATHÉMATIQUE

Problème aux limites à la dérivée tangentielle pour l'équation du type elliptique

par

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Le problème aux limites, proposé par W. Pogorzelski [1], consiste dans la recherche d'une fonction $u(x,y)$ harmonique à l'intérieur d'un domaine D limité par une courbe fermée C, qui sur cette courbe satisfait à une relation non-linéaire

$$\frac{du}{dn}+a(s)u=\Phi\left(s,u,\frac{du}{ds}\right) \tag{1}$$

entre les valeurs limites de la dérivée suivant la normale, du/dn, de la dérivée tangentielle du/ds et de la fonction $u(x,y)$; $a(s)$ est la fonction donnée de la longueur d'arc de la courbe C; $\Phi(s,u,t)$ est la fonction donnée de trois variables. Ce problème est la généralisation du problème aux limites de H. Poincaré [2], résolu complètement par B. Hvédélidzé [3]. Dans le présent travail nous nous proposons de résoudre le problème de la recherche d'une fonction $u(x,y)$ qui à l'intérieur du domaine D, limité par une courbe fermée C, satisfait à l'équation

$$\Delta u=\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}=F\left(x,y,u,\frac{\partial u}{\partial x},\frac{\partial u}{\partial y}\right) \tag{2}$$

et en tout point s au bord C vérifie la relation à la dérivée tangentielle (1).

On admet les suppositions suivantes:

I. La ligne fermée de Jordan C a la tangente continue en tout point, et l'angle que fait cette tangente avec une direction fixe satisfait à la condition de Hölder, c'est-à-dire qu'on a

$$|\delta_{ss_1}|\leqslant c|s-s_1|^{\gamma} \quad 0<\gamma\leqslant 1,$$

où δ_{ss_1} désigne l'angle que font les tangentes aux deux points arbitraires de la courbe C aux coordonnées curvilignes s et s_1.

II. La fonction des trois variables réelles $\Phi(s,u,t)$ est définie dans la région fermée

$$S \in C, \quad |u| \leqslant R_1, \quad |t| \leqslant R_2.$$

Elle vérifie la condition de Hölder par rapport aux variables s,u et la condition de Lipschitz par rapport à la variable t, c.-à-d.

$$|\Phi(s,u,t)-\Phi(s_1,u_1,t_1)| \leqslant K[|s-s_1|^{\alpha}+|u-u_1|^{\beta}+|t-t_1|].$$

III. La fonction donnée $F(x,y,u,v,w)$ est définie dans la région fermée

$$(x,y) \in D+C, \quad |u| \leqslant R_1, \quad |v| \leqslant R_2, \quad |w| \leqslant R_2$$

et vérifie la condition de Hölder par rapport aux variables x,y,u,v,w.

IV. La fonction $a(s)$ définie sur C vérifie la condition de Hölder $|a(s)-a(s_1)| \leqslant K_1|s-s_1|^{\alpha}$.

On admet que les exposants de Hölder satisfont aux inégalités

$$\alpha < \beta \leqslant 1, \quad \alpha < \gamma \leqslant 1.$$

Nous cherchons la fonction demandée $u(A)$ sous la forme

$$u(A) = -\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{AB}} F\left[B,u(B),\frac{\partial u}{\partial \xi},\frac{\partial u}{\partial \eta}\right]d\xi\,d\eta + \int_C \log\frac{1}{r_{A\sigma}}\mu(\sigma)\,d\sigma, \tag{3}$$

où $A(x,y)$ et $B(\xi,\eta)$ sont les deux points à l'intérieur du domaine D; $r_{A\sigma}$ désigne la distance entre les points $A(x,y)$ et $Q(\sigma)$ sur la courbe C, et $\mu(\sigma)$ est la densité inconnue du potentiel logarithmique de la couche simple.

En demandant que la fonction (3) vérifie la relation limite (1) on arrive à l'équation

$$\begin{aligned} -\pi\mu(s) + \int_C \frac{\sin\varphi_{s\sigma}}{r_{s\sigma}}\mu(\sigma)\,d\sigma + a(s)\int_C \log\frac{1}{r_{s\sigma}}\mu(\sigma)\,d\sigma = \\ = \Phi\Big\{s, -\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{sB}} F\left[B,u(B)\frac{\partial u}{\partial \xi},\frac{\partial u}{\partial \eta}\right]d\xi\,d\eta + \int_C \log\frac{1}{r_{s\sigma}}\mu(\sigma)\,d\sigma, \\ -\frac{1}{2\pi}\int_D\int \frac{\cos\varphi_{sB}}{r_{sB}} F\left[B,u(B),\frac{\partial u}{\partial \xi},\frac{\partial u}{\partial \eta}\right]d\xi\,d\eta + \int_C \frac{\cos\varphi_{s\sigma}}{r_{s\sigma}}\mu(\sigma)\,d\sigma\Big\} + \\ + \frac{1}{2\pi}\int_D\int \frac{\sin\varphi_{sB}}{r_{sB}} F\left[B,u(B)\frac{\partial u}{\partial \xi},\frac{\partial u}{\partial \eta}\right]d\xi\,d\eta + \frac{a(s)}{2\pi}\int_D\int \log\frac{1}{r_{sB}} F\left[B,u(B),\frac{\partial u}{\partial \xi},\frac{\partial u}{\partial \eta}\right]d\xi\,d\eta. \end{aligned} \tag{4}$$

C'est une équation intégro-différentielle non-linéaire à forte singularité, puisque la fonction $\frac{\cos\varphi_{s\sigma}}{r_{s\sigma}}$ admet une forte singularité si $r_{s\sigma}\to 0$. Notre problème est donc ramené à la résolution du système des deux équations intégrales (3) et (4) aux deux fonctions inconnues $u(A)$ et $\mu(s)$.

Pour résoudre ce système nous allons résoudre le système auxiliaire d'équations intégrales aux quatre fonctions inconnues, $u(A)$, $v(A)$, $w(A)$, $\mu(s)$:

$$
\begin{aligned}
u(A) &= -\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{AB}}F[B,u(B),v(B),w(B)]\,d\omega_B+\int_C \log\frac{1}{r_{A\sigma}}\mu(\sigma)\,d\sigma,\\
v(A) &= \frac{1}{2\pi}\int_D\int \frac{x-\xi}{r_{AB}^2}F[B,u(B),v(B),w(B)]\,d\omega_B-\int_C \frac{x-\xi_\sigma}{r_{A\sigma}^2}\mu(\sigma)\,d\sigma,\\
w(A) &= \frac{1}{2\pi}\int_D\int \frac{y-\eta}{r_{AB}^2}F[B,u(B),v(B),w(B)]\,d\omega_B-\int_C \frac{y-\eta_\sigma}{r_{A\sigma}^2}\mu(\sigma)\,d\sigma,\\
&-\pi\mu(s)+\int_C \frac{\sin\varphi_{s\sigma}}{r_{s\sigma}}\mu(\sigma)\,d\sigma+a(s)\int_C \log\frac{1}{r_{s\sigma}}\mu(\sigma)\,d\sigma=\\
=\Phi\Big\{s,\ &-\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{SB}}F[B,u(B),v(B),w(B)]\,d\omega_B+\int_C \log\frac{1}{r_{s\sigma}}\mu(\sigma)\,d\sigma,\\
&\frac{1}{2\pi}\int_D\int \frac{\cos\varphi_{sB}}{r_{sB}}F[B,u(B),v(B),w(B)]\,d\omega_B+\int_C \frac{\cos\varphi_{s\sigma}}{r_{s\sigma}}\mu(\sigma)\,d\sigma\Big\}+\\
&+\frac{1}{2\pi}\int_D\int \frac{\sin\varphi_{sB}}{r_{sB}}F[B,u(B),v(B),w(B)]\,d\omega_B+\\
&+\frac{a(s)}{2\pi}\int_D\int \log\frac{1}{r_{sB}}F[B,u(B),v(B),w(B)]\,d\omega_B,
\end{aligned}
\tag{5}
$$

ξ_σ,η_σ désignant les coordonnées du point $Q(\sigma)$ de la courbe C. Pour résoudre le système d'équations (5) considérons l'espace A de Banach composé de tous les systèmes de quatre fonctions continues réelles $U[u(A),v(A),w(A),\mu(s)]$, déterminées dans le domaine $D+C$. Soit dans cet espace un ensemble E de tous les points $U[u(A),v(A),w(A),\mu(s)]$ satisfaisant aux conditions

$$
\begin{cases}
|u(A)|\leqslant R_1; \quad |v(A)|\leqslant R_2; \quad |w(A)|\leqslant R_2,\\
|\mu(s)\leqslant \varrho; \quad |\mu(s)-\mu(s_1)\leqslant \varkappa|s-s_1|^\alpha,
\end{cases}
\tag{6}
$$

où α est une constante dans les suppositions II et IV. Les constantes ϱ et $\varkappa$ sont fixées arbitrairement. L'ensemble E est évidemment fermé et convexe. Transformons maintenant l'ensemble E en faisant correspondre

à tout point $U[u(A),v(A),w(A),\mu(s)]$ de cet ensemble le point $\bar{U}[\bar{u}(A), \bar{v}(A),\bar{w}(A),\bar{\mu}(s)]$ de l'espace Λ déterminé par les relations fonctionnelles:

$$\bar{\mu}(A) = -\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{AB}} F[B,u(B),v(B),w(B)]\,d\omega_B + \int_C \log\frac{1}{r_{A\sigma}}\,\mu(\sigma)\,d\sigma,$$

$$\bar{v}(A) = \frac{1}{2\pi}\int_D\int \frac{x-\xi}{r_{AB}^2} F[B,u(B),v(B),w(B)]\,d\omega_B - \int_C \frac{x-\xi_\sigma}{r_{A\sigma}^2}\mu(\sigma)\,d\sigma,$$

$$\bar{w}(A) = \frac{1}{2\pi}\int_D\int \frac{y-\eta}{r_{AB}^2} F[B,u(B),v(B),w(B)]\,d\omega_B - \int_C \frac{y-\eta_\sigma}{r_{A\sigma}^2}\mu(\sigma)\,d\sigma,$$

$$-\pi\bar{\mu}(s) + \int_C \frac{\sin\varphi_{s\sigma}}{r_{s\sigma}}\bar{\mu}(\sigma)\,d\sigma + a(s)\int_C \log\frac{1}{r_{s\sigma}}\bar{\mu}(\sigma)\,d\sigma =$$

(7)

$$= \Phi\Big\{s, -\frac{1}{2\pi}\int_D\int \log\frac{1}{r_{SB}} F[B,u(B),v(B),w(B)]\,d\omega_B + \int_C \log\frac{1}{r_{s\sigma}}\,\mu(\sigma)\,d\sigma,$$

$$\frac{1}{2\pi}\int_D\int \frac{\cos\varphi_{sB}}{r_{sB}} F[B,u(B),v(B),w(B)]\,d\omega_B + \int_C \frac{\cos\varphi_{s\sigma}}{r_{s\sigma}}\,\mu(\sigma)\,d\sigma\Big\} +$$

$$+\frac{1}{2\pi}\int_D\int \frac{\sin\varphi_{sB}}{r_{sB}} F[B,u(B),v(B),w(B)]\,d\omega_B +$$

$$+\frac{a(s)}{2\pi}\int_D\int \log\frac{1}{r_{sB}} F[B,u(B),v(B),w(B)]\,d\omega_B.$$

La quatrième équation (7) a la forme d'une équation de Fredholm à faible singularité avec la fonction inconnue $\bar{\mu}(s)$. Nous supposons que l'équation intégrale homogène, obtenue en égalant à zéro le côté droit de cette équation, n'a qu'une solution $\bar{\mu}=0$; alors à chaque point $U[u(A),v(A),w(A),\mu(s)]$ de l'ensemble E correspond un point $\bar{U}[\bar{u}(A),\bar{v}(A),\bar{w}(A),\bar{\mu}(s)]$ de l'espace Λ.

D'après les théorèmes de W. Pogorzelski [1] concernant les intégrales curvilignes, et les théorèmes de l'auteur [5] concernant les intégrales doubles dans la quatrième équation (7), nous concluons que la fonction $\bar{\mu}(s)$ correspondant aux fonctions $u(A),v(A),w(A),\mu(s)$ de l'ensemble E satisfait à la condition de Hölder avec l'exposant α.

Nous constatons ensuite que la transformation (7) est continue et que le point transformé $[\bar{u}(A),\bar{v}(A),\bar{w}(A),\bar{\mu}(s)]$ fera partie de l'ensemble E si les bornes supérieures des fonctions $|F|$ et $|\Phi|$ et le coefficient de Hölder K, sont suffisamment petites.

Enfin on peut démontrer que les fonctions transformées $\bar{u}(A),\bar{v}(A),\bar{w}(A),\bar{\mu}(s)$ sont équicontinues et équibornées; elles vérifient donc les conditions du théorème d'Arzelà et l'ensemble transformé $\bar{E}$ est compact.

Toutes les conditions du théorème de J. Schauder [4] étant satisfaites, nous concluons que dans l'ensemble E il existe au moins un point $U[u^*(A),v^*(A),w^*(A),\mu^*(s)]$ invariant relativement à la transforma-

tion (7), c.-à-d. vérifiant le système d'équations intégrales (5). Par le calcul simple nous obtenons que $v^*(A)=\frac{\partial u^*(A)}{\partial x}$, $w^*(A)=\frac{\partial u^*(A)}{\partial y}$; cela veut dire que les fonctions obtenues $u^*(A)$ et $\mu^*(s)$ vérifient les équations intégro-différentielles (3) et (4). D'après l'équation intégrale (4) on voit que la fonction $u^*(A)$ vérifie la condition limite (1) en tout point de la courbe C. La fonction $u^*(A)$ vérifie aussi l'équation donnée (2) puisqu'on peut démontrer que la fonction $F\left[B, u^*(B), \frac{\partial u^*(B)}{\partial \xi}, \frac{\partial u^*(B)}{\partial \eta}\right]$ vérifie la condition de Hölder dans tout domaine fermé $D^* \subset D$.

Un développement plus détaillé des considérations précédentes sera publié sous le même titre dans Annales Polonici Mathematici, 1957.

INSTITUT MATHÉMATIQUE DE L'ACADÉMIE POLONAISE DES SCIENCES

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MATHEMATICS

On the Distribution of the Values of a Class of Arithmetical Functions

by

SHAO PIN-TSUNG

Presented by W. SIERPIŃSKI on June 14, 1956

1. By making use only of simple and elementary methods, A. Schinzel and W. Sierpiński obtained very interesting results [1], [2] concerning the distribution of the values of Euler's function $\varphi(n)$ and that of the function $\sigma(n)$ which represents the sum of all divisors of n.

It is Professor Hua Loo-Keng who first pointed out that by Brun's method much more elaborate results concerning the distribution of the values of Euler's function $\varphi(n)$ may be obtained. Following his suggestions, Wang Yuan, reccently suceeded in writing a very fine paper containing these results.

The author, under Professor Min Szu-Hoa's supervision, is now able to prove, using Brun's method, that not only the function $\sigma(n)$ but actually a very large class of arithmetical functions share with $\varphi(n)$ the same interesting properties established by Wang only for $\varphi(n)$. It is also worth while mentioning that the method used is an adaptation of that used by the author in solving a problem left open by Schinzel [2] concerning the divisor function $\tau(n)$.

Definition 1. Let $f_s(n)$ be a positive multiplicative function satisfying the following conditions.

1. Let p denote a prime. Then for every positive integer l we have

$$\lim_{p\to\infty}\frac{f_s(p^l)}{p^{ls}}=1.$$

2. Let (a,b) denote the set of all real numbers x in the interval $a<x<b$. Suppose that for every real number $\varepsilon_0>0$, an arbitrary positive integer M, and any number $\alpha\in(a,b)$, there exists always a positive integer N such that $(M,N)=1$ and

$$\left|\frac{f_s(N)}{N^s}-\alpha\right|<\varepsilon_0.$$

3. For any set of non-negative real numbers $\delta_0,\dots,\delta_{k-1}$ and $\varepsilon_0>0$, there exists always a sequence of real numbers, $\alpha_\nu \in (a,b)$ $(\nu=0,1,\dots,k)$, such that

$$\left|\delta_\nu-\frac{\alpha_\nu}{\alpha_{\nu+1}}\right|<\varepsilon_0, \qquad (\nu=0,1,\dots,k-1).$$

Then $f_s(n)$ will be called a function of class C-Mf and we write

$$f_s(n) \in C\text{-}Mf.$$

It can be easily verified that for $0<s\leqslant 1$ the multiplicative functions

$$\varphi_s(n)=n^s\left(1-\frac{1}{p_1^s}\right)\dots\left(1-\frac{1}{p_k^s}\right) \quad (\text{for } n=p_1^{a_1},\dots,p_k^{a_k})$$

and

$$\sigma_s(n)=\sum_{d|n} d^s,$$

etc. satisfy these conditions, i. e.,

$$\varphi_s(n) \in C\text{-}Mf \qquad \sigma_s(n)\ \varepsilon\ C\text{-}Mf, \text{ etc.}$$

Definition 2. Let the arithmetical function $\Omega_s(n)$ satisfy the following conditions:

1. For $(n_1,n_2)=1$ we have

$$\Omega_s(n_1n_2)=\Omega_s(n_1)+\Omega_s(n_2),$$

2. Let p denote a prime, then

$$0\leqslant\Omega_s(p^a)\leqslant k=k(s,c) \quad \text{for} \quad a\leqslant c,$$

and

$$\Omega_s(p)=1, \quad \Omega_s(1)=0.$$

Then $\Omega_s(n)$ will be called a function of class Af and we write

$$\Omega_s(n) \in Af.$$

It can be easily verified that the arithmetical functions

$$\Omega(n)=\alpha_1+\dots+\alpha_k \qquad (\text{for} \quad n=p_1^{a_1}\dots p_k^{a_k})$$

and

$$\omega(n)=\sum_{p|n} 1$$

satisfy these conditions, i. e.,

$$\Omega(n) \in Af, \quad \omega(n) \in Af.$$

Theorem 1. *If the arithmetical function $G_s(n)$ satisfies $G_s(n) \in C\text{-}Mf$ or $G_s(n) \in Af$, then, given any $\varepsilon>0$, and any sequence of non-negative real numbers $\delta_0,\dots,\delta_{k-1}$, we can always find a natural n such that*

$$\left|\frac{G_s(n+\nu)}{G_s(n+\nu+1)}-\delta_\nu\right|<\varepsilon \quad (\nu=0,1,\dots,k-1). \tag{1}$$

More precisely, if we denote the number of integers n $(1 \leqslant n \leqslant x)$, *satisfying* (1) *by* $N^*(x)$, *then for sufficiently large* x, *we have*

$$N^*(x) > C^* \frac{x}{\log^{k+1} x}, \tag{2}$$

where $C^* = C^*(k; \delta_0, \ldots, \delta_{k-1}; \varepsilon, s)$ *is a positive constant, independent of* x

The theorem includes Wang's result mentioned previously as a special case and may also be regarded as both a generalisation of and an improvement on Schinzel's result [2].

The proofs of these results will be published under the title: *On the Distribution of the Values of a Class of Arithmetical Functions*, which will soon appear in Acta Scientiarum Naturalium Universitatis Pekinensis.

2. Let s be any positive integer $\geqslant 2$, and

$$\tau_s(n) = \sum_{x_1 \ldots x_s = n} 1.$$

We have

THEOREM 2. *For every positive integer* k *and every sequence of positive integers* $\delta_0, \delta_1 \ldots \delta_{k-1}$, *there exists a natural number* $n > 1$ *such that*

$$\delta_\nu \leqslant \tau_s(n+\nu) \leqslant C_0 \delta_\nu, \quad (\nu = 0, 1, \ldots, k-1), \tag{3}$$

where $C_0 = C_0(k, s)$ *is a positive constant.*

More precisely, if we denote the number of integers n, *in the interval* $1 \leqslant n \leqslant x$, *satisfying* (3) *by* $N'(x)$, *then for sufficiently large* x, *we have*

$$N'(x) > C' \frac{x}{\log^k x}, \tag{4}$$

where $C' = C'(k; \delta_0, \delta_1, \ldots, \delta_{k-1}; s)$ *is a positive constant independent of* x.

THEOREM 3. *For every positive integer* k *and every sequence of positive real numbers* $B_0, B_1, \ldots, B_{k-1}$, *we can always find a natural number* $n > 1$ *such that*

$$C_1 B_\nu \leqslant \frac{\tau_s(n+\nu)}{\tau_s(n+\nu+1)} \leqslant C_2 B_\nu, \quad (\nu = 0, 1, \ldots, k-1), \tag{5}$$

where $C_1 = C_1(k, s)$ *and* $C_2 = C_2(k, s)$ *are positive constants.*

More precisely, if we denote by $N(x)$ *the number of integers* n, *in the interval* $1 \leqslant n \leqslant x$, *satisfying* (5), *then for sufficiently large* x, *we have*

$$N(x) > C_3 \frac{x}{\log^{k+1} x}, \tag{6}$$

where $C_3 = C_3(k; B_0, B_1, \ldots, B_{k-1}; s)$ *is a positive constant independent of* x.

The case $s = 2$ gives a solution of Schinzel's problem [2].

The proofs of these results will be published under the title: *On a Problem of Schinzel.*

Note added Feb. 23, 1956. I was informed that A. Schinzel obtained independently the result concerning $\tau(n)$, as proved by myself in this paper, and that he also obtained the result concerning $\sigma(n)$ which is, in fact, a special case of our Theorem 1. I was also informed that Wang has written a paper with Schinzel, containing all their results mentioned above. Their joint paper will appear in Annales Polonici Mathematici (cf. [3]).

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MATHEMATICS

On the Imbedding of Polyhedrons in Euclidean Spaces

by

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Presented by K. BORSUK on June 19, 1956

1. For the imbedding or realisation of complexes or more general spaces in Euclidean spaces we may cite the following known results:

(a) In 1932, van Kampen [1] (also Flores [2]) proved the existence of n-dimensional finite complexes not (rectilinearly) realisable in Euclidean space of dimension $2n$.

(b) In the case of differentiable manifolds M. Whitney [3] has introduced a system of invariants $\overline{W}^m \in H^m(M, \text{mod } 2)$ and proved that

$$\overline{W}^k = 0, \quad k \geqslant m - n \tag{1}$$

are necessary conditions for an n-dimensional closed differentiable manifold to be (differentiably) realisable in R^m.

(c) For compact Hausdorff spaces X, Thom ([4], Theorem III. 25) has proved the following theorem: Let

$$Q^i : H^r(X, \text{mod } 2) \to H^{r+1}(X, \text{mod } 2)$$

be certain operations deduced from Steenrod squares, then

$$Q^i H^r(X, \text{mod } 2) = 0, \; 2i + r \geqslant m \tag{2}$$

are necessary conditions for X to be (topologically) realisable in R^m.

In the various theories listed above, not only the methods used are quite different from each other, but also the domain of spaces considered and the realisation concepts involved are not the same. In what follows we shall show that these theories, so different in appearance, are merely the particular phases of a more general theory.

2. Let us recall some facts about the theory of P. A. Smith [5] concerning spaces *) under periodic transformations. Let $\widetilde{Y}$ be a space and t a homeomorphism of $\widetilde{Y}$ into itself without fixed points and of period 2.

*) By spaces we shall always mean Hausdorff spaces.

Let $Y=\tilde{Y}/t$ be the space of orbits of $\tilde{Y}$ under t and $\pi:\tilde{Y}\to Y$ the natural projection, so that $\tilde{Y}$ is a two-sheeted covering space of Y with projection π. With respect to the pair $(\tilde{Y},t)$ or the triple $(\tilde{Y},Y,\pi)$ we may define according to P. A. Smith a system of cohomology classes

$$A^m(\tilde{Y},Y,\pi)=A^m(\tilde{Y},t)\in H^m(Y,I_{(m)}),\quad m\geqslant 0,$$

where $I_{(m)}=$ group of integers I for m even, $I_{(m)}=$ group I_2 of integers mod 2 for m odd, and H represents a singular homology system. If $(\tilde{Y}',t')$ is another such pair with corresponding projection $\pi':\tilde{Y}'\to Y'=\tilde{Y}'/t'$, and $\tilde{f}:\tilde{Y}\to\tilde{Y}'$, $f:Y\to Y'$ are maps such that $\pi'\tilde{f}=f\pi$, then $(\tilde{f},f):(\tilde{Y},Y,\pi)\to(\tilde{Y}',Y',\pi')$ will be called simply a map. For such a map, we have then

$$f^*A^m(\tilde{Y}',Y',\pi')=A^m(\tilde{Y},Y,\pi),\quad m\geqslant 0. \tag{3}$$

Now, for any space X let $\tilde{X}^*$ be the space of all ordered pairs (x_1,x_2) and X^* the space of all non-ordered pairs $\{x_1,x_2\}$, where $x_1,x_2\in X$ and $x_1\neq x_2$. If $t:\tilde{X}^*\to\tilde{X}^*$ denotes the transformation $t(x_1,x_2)=(x_2,x_1)$ and $\pi:\tilde{X}^*\to X^*$ the projection $\pi(x_1,x_2)=\{x_1,x_2\}$, then we have a pair $(\tilde{X}^*,t)$ or a triple $(\tilde{X}^*,X^*,\pi)$, which (and hence also the classes $A^m(\tilde{X}^*,X^*,\pi)=A^m(\tilde{X}^*,t)$) depend evidently only on the topological type of the space X. We may therefore denote these classes by

$$\Phi^m(X)\in H^l(X^*,I_{(m)}).$$

Our theory may then be formulated in terms of the following

Main theorem. *For a space X to be topologically realisable in a Euclidean space R^m of dimension m it is necessary that*

$$\Phi^m(X)=0. \tag{4}$$

Proof. Suppose that X is realisable in R^m and g is such a realisation. Let S^{m-1} be the unit sphere in R^m, and t' the antipodal map of S^{m-1} so that S^{m-1}/t' is an $(m-1)$-dimensional projective space P^{m-1}, for which the projection $S^{m-1}\to P^{m-1}$ will be denoted by π'. Now for any point $(x_1x_2)\in\tilde{X}^*$ let us draw a half-line through the origin of R^m, parallel to the line joining $g(x_1)$ and $g(x_2)$ and pointing in the same direction from $g(x_1)$ to $g(x_2)$. Denote the point of intersection of this half-line with S^{m-1} by $\tilde{f}(x_1,x_2)$ and the point $\pi'\tilde{f}(x_1,x_2)$ by $f\{x_1,x_2\}$, then we get a map

$$(\tilde{f},f):(\tilde{X}^*,X^*,\pi)\to(S^{m-1},P^{m-1},\pi').$$

As $A^m(S^{m-1},P^{m-1},\pi')$ is evidently 0, we get (4) from (3).

That the theorems of Whitney and Thom (the latter in the case of finite polyhedrons only) are both consequences of the above main theorem may be seen from the following two propositions:

Theorem 1. *Let X be a closed differentiable manifold of dimension n, then* (1) *is a consequence of* (4).

THEOREM 2. *For any finite polyhedron* X, (2) *is a consequence of* (4).

The proofs of these two theorems are too complicated to be given here. We shall restrict ourselves to the following remarks:

1° Examples may be constructed which show, in the case of closed differentiable manifolds, that neither (1) is a consequence of (2), nor (2) is a consequence of (1). It follows that even in the case of differentiable realisation of differentiable manifolds, the methods of Whitney and Thom are quite independent of one another, while both of them may be deduced from our main theorem.

2° Our main theorem shows that Whitney's condition (1) is necessary not merely for the *differentiable* realisation of the differentiable manifold in the corresponding Euclidean space, but also for the *topological* realisation.

3. Consider now the connection between our theory and that of van Kampen [6].

For this purpose let us consider a finite polyhedron X with a simplicial subdivision K, its reduced product $\tilde{K}^*$ formed by cells of the form $\sigma \times \tau$ with $\sigma, \tau \in K$ having no common vertices and its reduced symmetric product K^* obtained from $\tilde{K}^*$ by the identification of each pair $\sigma \times \tau$ and $\tau \times \sigma$ into the same cell $\sigma * \tau$ (or $\tau * \sigma$). If we orient $\sigma * \tau$ as the usual product $\sigma \times \tau$, then algebraically we would have

$$\sigma * \tau = (-1)^{\dim\sigma \dim\tau} \tau * \sigma. \tag{5}$$

As the complex $\tilde{K}^*$ is a two-sheeted covering complex over K^* with natural projection, say ω, the triple *) $(|\tilde{K}^*|, |K^*|, \omega)$ gives rise to a system of classes $\Phi^m(K) = A^m(|\tilde{K}^*|, |K^*|, \omega) \in H^m(|K^*|, I_{(m)})$. It is easy to see that $(|\tilde{K}^*|, |K^*|, \omega)$ is a "deformation retract" of $(\tilde{X}^*, X^*, \pi)$ so that we have canonically

$$H^m(|K^*|, I_{(m)}) \approx H^m(X^*, I_{(m)}), \tag{6}$$

and $\Phi^m(K), \Phi^m(X)$ correspond under this isomorphism.

Let us now try to imbed rectilinearly K in R^m as far as possible, so that under such a "pseudo-imbedding", say f, the images $f\sigma, f\tau$ of every pair of simplexes σ, τ of K, having no common vertices and with $\dim\sigma + \dim\tau \leqslant m$, are always Euclidean simplexes in general position. For any cell $\sigma * \tau \in K^*$ of dimension m, $f\sigma$ and $f\tau$ then have a well-defined index of intersection, $I(f\sigma, f\tau)$, with respect to a fixed orientation of R^m.

In view of (5), the equations $\varphi_f(\sigma * \tau) = (-1)^{\dim\sigma} \varrho_{(m)} I(f\sigma, f\tau)$, in which $\varrho_{(m)}$ is the identity for m = even and reduction mod 2 for m = odd, then define consistently an m-dimensional co-chain φ_f of K^* on the coefficient group $I_{(m)}$. This co-chain may serve as a primary measure of the deviation of the pseudo-imbedding f from a true one. We then have the following

*) We denote the space of a complex K by $|K|$.

THEOREM 3. *The co-chain φ_f associated to a pseudo-imbedding $f: K \to R^m$ is always a co-cycle with its co-homology class $\Phi^m(K) \in H^m(|K^*|, I_{(m)})$, independent of the pseudo-imbedding f chosen, and coincides with $\Phi^m(X)$ under the natural isomorphism* (6).

For $\dim K = n$ and $m = 2n$ the class $\Phi^{2n}(X)$ is in reality the same as the original van Kampen invariant introduced by him to establish his theorem. It follows that from our main theorem, as well as from Theorem 3, we get van Kampen's theorem in this extreme case.

Remark. Even in this extreme case our theorem contains a little more than that of van Kampen in the sense that $\Phi^{2n} = 0$ is necessary not only for *rectilinear* realisability of a certain subdivision of X in R^{2n}, but also for the *topological* realisation of X in R^{2n}.

4. In certain extreme cases the condition (4) in our main theorem is not only necessary, but also sufficient for X to be realisable in R^m. In fact, we have

THEOREM 4. *If X is a finite polyhedron of dimension $n > 2$, then*

$$\Phi^{2n}(X) = 0$$

is a necessary and sufficient condition for X to be realisable in R^{2n}.

This theorem furnishes us an intrinsic characterisation of n-dimensional finite polyhedrons in $2n-$dimensional Euclidean spaces ($n > 2$). Our proof depends on the realisability ([6], Theorem 7) of every co-cycle in $\Phi^{2n}(K)$ (X is a finite polyhedron with a simplicial subdivision K) as a co-cycle φ_f defined in par. 3 and also on some special device used by Whitney [7] to prove his theorem stating that every $n-$dimensional differentiable manifold is differentiably realisable in R^{2n}.

Theorem 4 remains true in case $n = 1$, as follows easily from a well-known theorem of Kuratowski [8] about planar Peano continuum. In fact, this theorem may be reformulated in the following form:

THEOREM 4'. *For a Peano continuum X to be planar it is necessary and sufficient that $\Phi^2(X) = 0$.*

In particular, when X is a finite linear graph, this gives us a "quantitative" criterion of its planarity and also effective means to determine it in a finite number of steps, in contrast to the original "qualitative" criterion of Kuratowski (also Whitney, MacLane and perhaps others).

Remark. The case when $n = 2$ has not yet been settled.

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MATHÉMATIQUE

Sur une généralisation des problèmes classiques concernant un système d'équations différentielles hyperboliques du second ordre à deux variables indépendantes

par

Z. SZMYDT

Présenté par T. WAŻEWSKI le 23 Juin 1956

Cette communication a pour but d'avancer notre généralisation, donnée antérieurement [3], des problèmes classiques concernant le système de n équations différentielles du second ordre,

$$(1) \qquad u^{(i)}_{xy}(x,y)=f^{(i)}(x,y,u^{(1)},\dots,u^{(n)},u^{(1)}_x,\dots,u^{(n)}_x,u^{(1)}_y,\dots,u^{(n)}_y) \qquad (i=1,\dots,n),$$

aux membres droits continus.

1. Désignons par D le rectangle défini par les inégalités

$$(2) \qquad -\alpha\leqslant x\leqslant\alpha \quad \text{et} \quad -\beta\leqslant y\leqslant\beta, \quad \text{où} \quad 0<\alpha<\infty \quad \text{et} \quad 0<\beta<\infty.$$

Considérons $2n$ courbes continues Γ_i et Λ_i situées dans le rectangle D et définies par les équations respectives

$$y=\gamma_i(x) \quad \text{lorsque} \quad -\alpha\leqslant x\leqslant\alpha,$$
$$x=\lambda_i(y) \quad \text{lorsque} \quad -\beta\leqslant y\leqslant\beta,$$

pour $i=1,\dots,n$.

Appelons *problèmes du type* T^* ceux qui concernent l'existence d'une solution $U(x,y)=(u^{(1)}(x,y),\dots,u^{(n)}(x,y))$ du système (1) ayant les dérivées U_x, U_y, U_{xy} continues dans le rectangle D et satisfaisant le long des $2n$ courbes Γ_i et Λ_i à certaines relations données.

Soit

$$U=(u^{(1)},\dots,u^{(n)}),\ P=(p^{(1)},\dots,p^{(n)}),\ Q=(q^{(1)},\dots,q^{(n)}),\ F=(f^{(1)},\dots,f^{(n)}).$$

Il est évident que les problèmes du type T envisagés dans la communication [3] précitée sont du type T^* restreint par les conditions

$$(3) \qquad \begin{aligned} &\gamma_1(x)\equiv\dots\equiv\gamma_n(x) \quad \text{lorsque} \quad -\alpha\leqslant x\leqslant\alpha,\\ &\lambda_1(y)\equiv\dots\equiv\lambda_n(y) \quad \text{lorsque} \quad -\beta\leqslant y\leqslant\beta. \end{aligned}$$

Tous les problèmes classiques (dits de Darboux, de Cauchy, de Picard, de Goursat et mixtes) sont donc du type T^*, puisqu'ils sont du type T.

Voici maintenant un problème du type T^* assez général:

PROBLÈME I*. Existe-t-il une solution $U(x,y)=(u^{(1)}(x,y),\dots,u^{(n)}(x,y))$ du système (1) ayant les dérivées U_x, U_y, U_{xy} continues dans le rectangle D et satisfaisant pour $i=1,\dots,n$ aux conditions

$$u^{(i)}(\mathring{x}_i,\mathring{y}_i)=\mathring{u}^{(i)},$$

$$u_x^{(i)}(x,y)=g^{(i)}(x,U(x,y),U_y(x,y)) \quad \text{pour} \quad y=\gamma_i(x), \quad -\alpha\leqslant x\leqslant\alpha,$$

$$u_y^{(i)}(x,y)=h^{(i)}(y,U(x,y),U_x(x,y)) \quad \text{pour} \quad x=\lambda_i(y), \quad -\beta\leqslant y\leqslant\beta,$$

où $(\mathring{x}_i,\mathring{y}_i)$ sont des points arbitrairement choisis dans le rectangle D, $U=(\mathring{u}^{(1)},\dots,\mathring{u}^{(n)})$ est un vecteur constant et $G(x,U,Q)=(g^{(1)}(x,U,Q),\dots,g^{(n)}(x,U,Q))$ et $H(y,U,P)=(h^{(1)}(y,U,P),\dots,h^{(n)}(y,U,P))$ sont des fonctions continues données d'avance *).

L'existence et l'unicité des solutions des problèmes du type T^* peuvent être démontrées par la méthode indiquée dans [3] pour les problèmes du type T. Nous l'avons signalé pour la première fois à la conférence sur le équations différentielles aux dérivées partielles (Cracovie, 26. IX — 1. X 1955) en indiquant comme exemple le problème I* dans lequel les fonctions $g^{(i)}$ et $h^{(i)}$ ne dépendaient que de x et y respectivement. La méthode de la démonstration est basée sur le lemme suivant, assez facile à établir.

LEMME I. *Si la fonction*

$$F(x,y,U,P,Q)=(f^{(1)}(x,y,U,P,Q),\dots,f^{(n)}(x,y,U,P,Q))$$

est continue, l'existence d'une solution du problème I équivaut à celle d'une solution de classe C^1 du système*

$$U(x,y)=\mathcal{L}[U], \tag{4}$$

où l'opérateur $\mathcal{L}[U]=(l^{(1)}[U],\dots,l^{(n)}[U])$ est défini par les formules

$$l^{(i)}[U]=\mathring{u}^{(i)}+\int_{\mathring{x}_i}^{x} g^{(i)}[s,U(s,\gamma_i(s)),U_y(s,\gamma_i(s))]\,ds+$$

$$+\int_{\mathring{y}_i}^{y} h^{(i)}[t,U(\lambda_i(t),t),U_x(\lambda_i(t),t)]\,dt-$$

$$+\int_{\mathring{x}_i}^{x}\left\{\int_{\gamma_i(s)}^{\mathring{y}_i} f^{(i)}[s,t,U(s,t),U_x(s,t),U_y(s,t)]\,dt\right\}ds+$$

$$+\int_{\mathring{y}_i}^{y}\left\{\int_{\lambda_i(t)}^{x} f^{(i)}[s,t,U(s,t),U_x(s,t),U_y(s,t)]\,ds\right\}dt$$

pour $i=1,\dots,n$.

) Dans le cas où les relations (3) sont satisfaites et $\mathring{x}_1=\dots=\mathring{x}_n$, $\mathring{y}_1=\dots=\mathring{y}_n$, le problème I coïncide avec le problème I de la communication [3].

2. Notations et hypothèses. Désignons par Π l'ensemble défini par les inégalités *)

$$(5)\qquad \begin{gathered} -\alpha \leqslant x \leqslant \alpha \quad \text{et} \quad -\beta \leqslant y \leqslant \beta, \quad \text{où} \quad 0<\alpha<\infty \quad \text{et} \quad 0<\beta<\infty, \\ |U| \leqslant r, \ |P| \leqslant r \quad \text{et} \quad |Q| \leqslant r \quad \text{où} \quad 0<r<\infty, \end{gathered}$$

et introduisons les deux ensembles suivants:

$$(6)\qquad -\alpha \leqslant x \leqslant \alpha, \quad |U| \leqslant r, \quad |Q| \leqslant r,$$

$$(7)\qquad -\beta \leqslant y \leqslant \beta, \quad |U| \leqslant r, \quad |P| \leqslant r.$$

Soit

$$(8)\qquad m = 2 \max(\alpha, \beta).$$

Hypothèse A. 1° *La fonction* $F(x,y,U,P,Q)$ *est continue dans l'ensemble* Π *défini par les formules* (5) *et satisfait à la condition* $N \leqslant \min\{r/m, r/m^2\}$, où

$$(9)\qquad N = \max_{(\Pi)} |F|.$$

2° *Le vecteur constant* $\mathring{U}$ *et les fonctions vectorielles continues* G *et* H *satisfont aux conditions*:

$$|\mathring{U}| \leqslant c \quad \text{et} \quad |G(x,U,Q)| \leqslant c \qquad \textit{dans l'ensemble (6)},$$

$$|H(y,U,P)| \leqslant c \qquad \textit{dans l'ensemble (7)},$$

où (cf. (8) *et* (9)) $c \leqslant \min\{r - mN, (r - Nm^2)/(1+2m)\}$.

3. Existence de la solution unique du problème I*.

Théorème 1. *Admettons l'hypothèse A et assujettissons les fonctions* F, G, H *aux conditions suivantes de Lipschitz*:

$$|F(x,y,U,P,Q) - F(x,y,\widetilde{U},\widetilde{P},\widetilde{Q})| \leqslant M\{|U-\widetilde{U}| + |P-\widetilde{P}| + |Q-\widetilde{Q}|\}$$
$$\textit{dans l'ensemble } \Pi,$$

$$|G(x,U,Q) - G(x,\widetilde{U},\widetilde{Q})| \leqslant K_1\{|U-\widetilde{U}| + |Q-\widetilde{Q}|\}$$
$$\textit{dans l'ensemble (6)},$$

$$|H(y,U,P) - H(y,\widetilde{U},\widetilde{P})| \leqslant K_2\{|U-\widetilde{U}| + |P-\widetilde{P}|\}$$
$$\textit{dans l'ensemble (7)}$$

pour des constantes mM (cf. (8)), K_1 et K_2 *suffisamment petites* **).

Alors le problème I a une seule solution* $U(x,y)$ ***).

---

*) La norme d'un vecteur $V = (v^{(1)}, \ldots, v^{(n)})$ étant donnée par la formule $|V| = \sup_{1 \leqslant i \leqslant n} |v^{(i)}|$.

**) Il suffit que $(1+m)(K_1 + K_2 + 2mM) < 1$.

***) Cette solution satisfait évidemment aux relations suivantes dans le rectangle D (cf. (2)): $|U(x,y)| \leqslant r$, $|U_x(x,y)| \leqslant r$, $|U_y(x,y)| \leqslant r$, $|U_{xy}(x,y)| \leqslant N$.

Le théorème 1 peut être démontré par la méthode des approximations successives, en posant (cf. lemme I):

$$\overset{1}{U}(x,y)=\mathring{U},$$
$$\overset{\nu+1}{U}(x,y)=\mathcal{L}[\overset{\nu}{U}] \quad \text{pour} \quad \nu=1,2,\ldots$$

4. On peut établir l'existence (mais pas l'unicité) d'une solution du problème I* en omettant dans le théorème 1 l'hypothèse que les fonctions $F(x,y,U,P,Q)$, $G(x,U,Q)$, $H(y,U,P)$ satisfont à des conditions de Lipschitz par rapport à la variable U *).

THÉORÈME 2. *Admettons l'hypothèse A et assujettissons les fonctions F,G,H aux conditions de Lipschitz*:

$$|F(x,y,U,P,Q)-F(x,y,U,\widetilde{P},\widetilde{Q})|\leqslant M\{|P-\widetilde{P}|+|Q-\widetilde{Q}|\} \quad \textit{dans l'ensemble } \Pi,$$
$$|G(x,U,Q)-G(x,U,\widetilde{Q})|\leqslant K_1|Q-\widetilde{Q}| \quad \textit{dans l'ensemble } (6),$$
$$|H(y,U,P)-H(y,U,\widetilde{P})|\leqslant K_2|P-\widetilde{P}| \quad \textit{dans l'ensemble } (7)$$

pour des constantes mM (cf. (8)) *et K_1K_2 satisfaisant aux inégalités*

$$mM<1 \quad \text{et} \quad K_1K_2<(1-mM)^2.$$

Alors il existe une solution du problème I.*

Pour démontrer le théorème 2, il suffit d'établir l'existence d'une solution de classe C^1 du système (4) (cf. lemme I) ou — ce qui revient au même — l'existence d'un point fixe de la transformation

$$\widetilde{U}=\mathcal{L}[U] \tag{11}$$

dans l'espace C^1. On y parvient en appliquant le théorème de Schauder ([2], Satz 1, p. 173) à la transformation (11) et à l'ensemble Z (contenu dans l'espace C^1) des fonctions $U(x,y)$ définies dans le rectangle D et y satisfaisant aux inégalités

$$|U(x,y)|\leqslant r, \quad |U_x(x,y)|\leqslant r, \quad |U_y(x,y)|\leqslant r,$$
$$|U_x(x,\bar{y})-U_x(x,\bar{\bar{y}})|\leqslant N|\bar{y}-\bar{\bar{y}}|, \quad |U_y(\bar{x},y)-U_y(\bar{\bar{x}},y)|\leqslant N|\bar{x}-\bar{\bar{x}}|,$$
$$|U_x(\bar{x},y)-U_x(\bar{\bar{x}},y)|\leqslant\psi(|\bar{x}-\bar{\bar{x}}|), \quad |U_y(x,\bar{y})-U_y(x,\bar{\bar{y}})|\leqslant\varphi(|\bar{y}-\bar{\bar{y}}|),$$

où $\psi(\varepsilon)$ et $\varphi(\varepsilon)$ sont des fonctions convenablement choisies qui tendent vers zéro avec ε. Nous nous dispensons de donner ici leurs définitions.

*) Un résultat analogue relatif au problème classique de Darboux, a été établi par P. Hartman et A. Wintner ([1] (I) p. 836) et d'une façon plus simple, à savoir en faisant usage de théorème de Schauder ([2], Satz 1, p. 173), par S. Mazur, au cours d'une séance du Groupe d'Analyse de l'Institut Mathématique de l'Académie Polonaise des Sciences à Varsovie en 1954.

5. HYPOTHÈSE A^{bis}. 1^0 *La fonction* $F(x,y,U,P,Q)$ *est continue et bornée dans l'ensemble* Π_1 *défini (dans l'espace de variables* x,y,U,P,Q*) par les relations*

$$-\alpha \leqslant x \leqslant \alpha, \quad -\beta \leqslant y \leqslant \beta \qquad \textit{(avec } U,P \textit{ et } Q \textit{ arbitraires).}$$

2^0 $G(x,U,Q)$ *et* $H(y,U,P)$ *sont des fonctions continues et bornées dans les ensembles* Σ_1 *et* Σ_2 *définis respectivement par les relations*

$$-\alpha \leqslant x \leqslant \alpha \qquad \textit{(avec } U \textit{ et } Q \textit{ arbitraires),}$$
$$-\beta \leqslant y \leqslant \beta \qquad \textit{(avec } U \textit{ et } P \textit{ arbitraires).}$$

Remarque 1. Dans les théorèmes 1 et 2 on peut substituer Π_1, Σ_1 et Σ_2 à Π, (6) et (7) respectivement, remplaçant en même temps l'hypothèse A par A^{bis}.

En effet, l'hypothèse A^{bis} étant admise, il existe un nombre r tel que relativement à l'ensemble Π l'hypothèse A est satisfaite *).

En appliquant la méthode des approximations successives à l'équation (4) on peut établir la partie de la remarque 1 concernant le théorème 1 sans que les fonctions F, G, H soient bornées.

Remarque 2. En remplaçant l'hypothèse (10) par une condition analogue à l'hypothèse K de ma communication [3], on peut établir, au moins dans certains cas, l'existence d'une solution du problème I*. Nous avons communiqué ces résultats à la séance du 15 mai 1956 de la Société Polonaise de Mathématique, Section de Cracovie.

6. Envisageons encore un autre problème du type T^*:

PROBLÈME II*. Existe-t-il une solution $U(x,y)=(u^{(1)}(x,y),\dots,u^{(n)}(x,y))$ du système (1) ayant les dérivées U_x, U_y, U_{xy} continues dans le rectangle D et satisfaisant pour $i=1,\dots,n$ aux conditions:

$$u_x^{(i)}(x,y)=g^{(i)}(x,U(x,y),\ U_y(x,y)) \quad \text{lorsque} \quad y=\gamma_i(x),\ -\alpha \leqslant x \leqslant \alpha,$$

$$u^{(i)}(\lambda_i(y),y)=\hat{u}^{(i)}+\int_{\mathring{y}_i}^{y} b^{(i)}\big[t,U(\lambda_i(t),t),\ U_x(\lambda_i(t),t)\big]\,dt \quad \text{lorsque} \quad -\beta \leqslant y \leqslant \beta,$$

où $\mathring{y}_i (i=1,\dots,n)$ sont des points arbitrairement choisis dans l'intervalle $[-\beta,\beta]$, $\hat{U}=(\hat{u}^{(1)},\dots,\hat{u}^{(n)})$ est un vecteur constant et $g^{(i)}(x,U,Q)$, $b^{(i)}(y,U,P)$ sont des fonctions continues données d'avance.

On vérifie facilement que le problème II* est équivalent pour $\lambda_i(y)$ de classe C^1 au problème I* dans lequel $\mathring{x}_i=\lambda_i(\mathring{y}_i)$ et $h^{(i)}(y,U,P)=b^{(i)}(y,U,P)-p^{(i)}\lambda_i'(y)$ pour $i=1,\dots,n$. Pourtant il est avantageux d'envi-

*) Il suffit que

$$r \geqslant \max\{c_1+mN_1,\ c_1(1+2m)+N_1m^2\} \quad \text{où} \quad c_1=\max\{\sup_{(\Sigma_1)}|G|,\ \sup_{(\Sigma_2)}|H|,\ |U|\},\quad N_1=\sup_{(\Pi_1)}|F|$$

et m est donné par (8).

sager le problème II* indépendamment du problème I*, tout comme le problème II de ma communication [3] y a été envisagé indépendamment du problème I (cf. [3] équation (4) et théorème 2).

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[1] P. Hartman and A. Wintner, *On hyperbolic partial differential equations*, Am. Jour. Math. **74** (1952), 834.

[2] J. Schauder, *Der Fixpunktsatz in Funktionalraümen*, Studia Math. **2** (1930), 171.

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MATHEMATICS

On Cyclic Ordering Relations

by

S. ŚWIERCZKOWSKI

Presented by H. STEINHAUS on June 29, 1956

1. A three-argument relation $[x,y,z]$, defined for x,y,z running over the set of integers, is called a *cyclic ordering relation* if it satisfies the following postulates:

I If x,y,z are different, then $[x,y,z]$ or $[x,z,y]$ holds, but not more than one of these relations is true.

II If $[x,y,z]$, then $[z,x,y]$.

III If $[x,y,z]$ and $[z,u,x]$, then $[u,y,z]$.

IV If $[x,y,z]$, then $[x+k,\ y+k,\ z+k]$ for $k=\pm 1,\ \pm 2,\ldots$

Let us put $N=\{0,1,\ldots,n\}$. A relation $[x,y,z]_N$ defined only for $x,y,z \in N$ and satisfying on this set all postulates I-IV is called a *partial cyclic ordering relation*. In this note we announce several theorems *) on such relations. Some of them were suggested by Professor Steinhaus.

THEOREM 1. *For every partial cyclic ordering relation* $[x,y,z]_N$, *there exists such a cyclic ordering relation* $[x,y,z]$ *that* $[x,y,z]_N \equiv [x,y,z]$ *for* $x,y,z \in N$.

2. Consider the partial cyclic ordering relation $[x,y,z]_N$. Two numbers $x_1,x_2 \in N$ are said to be *consecutive* if no $y \in N$ satisfies $[x_1,y,x_2]$.

THEOREM 2. *For every relation* $[x,y,z]_N$ *there are at most three values of the difference* x_2-x_1, *where* $x_1,x_2 \in N$ *are consecutive numbers.*

3. Given a real number ξ such that $k\xi$ is never an integer for $k \in N$ and $k>0$, we define a partial cyclic ordering relation $[x,y,z]^{\xi}_N$:

$$[x,y,z]^{\xi}_N \text{ is equivalent with the alternative}$$
$$(x\xi)<(y\xi)<(z\xi) \quad \text{or} \quad (y\xi)<(z\xi)<(x\xi) \quad \text{or} \quad (z\xi)<(x\xi)<(y\xi) \text{ **).}$$

THEOREM 3. *For any partial cyclic ordering relation* $[x,y,z]_N$ *there exists such a* ξ *that* $[x,y,z]_N \equiv [x,y,z]^{\xi}_N$ *for* $x,y,z\ N$.

*) The proofs will be published in Annales Polonici Mathematici.

**) $(u)=u-[u]$, where $[u]$=integral part of u.

4. Consider the partial cyclic ordering relation $[x,y,z]^{\xi}_{N}$. For two numbers $x_1, x_2 \in N$ we put

$$x_1 \dot{-} x_2 = \min \{|(x_1\xi)-(x_2\xi)|,\ 1-|(x_1\xi)-(x_2\xi)|\}\ *).$$

THEOREM 4. *For every relation $[x,y,z]^{\xi}_{N}$, there are at most three values of $x_1 \dot{-} x_2$, where $x_1, x_2 \in N$ are two consecutive numbers* **).

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*) Thus $x_1 \dot{-} x_2$ is the length of the shorter of the two arcs $\overset{\downarrow}{\frac{1}{2\pi} e^{2\pi i x_1 \xi}, \frac{1}{2\pi} e^{2\pi i x_2 \xi}}$, $\overset{\downarrow}{\frac{1}{2\pi} e^{2\pi i x_2 \xi}, \frac{1}{2\pi} e^{2\pi i x_1 \xi}}$ on the circle $|z| = \frac{1}{2\pi}$.

**) P. Erdös and P. Süsz have recently given a different proof after having been informed of the problem and the existence of the original proof.

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ASTRONOMY

On the Motion of B Stars in the Local System

by

M. KARPOWICZ

Presented by W. DZIEWULSKI on June 26, 1956

The motion of stars belonging to the Local System has been studied by several investigators [1]–[5] who concluded that these stars show certain kinematic features differing from those of stars not belonging to this group.

It seemed worth while to the author to undertake independent investigations based on the assumption that stars in the Local System move along circular orbits with angular velocity $\omega(R)$, where R is the distance of the star from the centre of the Local System; $\omega(R_0)$ and R_0 denote respectively the angular velocity and the distance of the Sun.

Under this assumption, the radial velocities observed, ΔV_r, of centroids of stars, may be represented by the well-known Camm function

$$f(RR_0)=R_0[\omega(R)-\omega(R_0)]=\frac{\Delta V_r}{\sin(l-l_0)\cos b},$$

where l and b are the galactic co-ordinates of centroids, l_0 — the galactic longitude of the centre of the Local System.

Assuming $l_0=240^0$ (in accordance with F. Seares' determination [6]), we obtain a set of values of $f(RR_0)$ for different stars grouped according to their R values. This set of $f(RR_0)$ represents a motion of stars in the Local System in relation to the Sun.

In the present case, only B stars were used, since the fact that they belong to the Local System seems certain. Data concerning radial velocities of these stars were collected from all available sources [7]–[11]. They were reduced to the centroid of stars near the Sun (assuming that the velocity of the Sun amounts to $V_0=22$ km./sec., $L_0=28^0$, $B_0=21$), and freed from the influence of galactic rotation by the aid of the Oort formula.

After rejecting stars of great latitudes ($|b|>25^0$), and of longitudes for which $\sin(l-l_0)$ is close to zero, I had 636 stars of known radial velocities, on which to base the present investigation.

The distances R were computed from the distance modules $m-M$, taking the M values from the table according to W. Becker [12].

Sp.	M_{viz}	M_{ph}
B0	−3.2	−3.4
B2	−2.3	−2.5
B4	−1.4	−1.5
B6	−0.8	−0.9
B8	0.0	0.0

The interstellar absorption was taken into account in accordance with the Parenago formula:

$$A(r,b)=\frac{a_0\beta}{\sin b}\left(1-e^{-\frac{r\sin b}{\beta}}\right),$$

where $a_0=3^m.4$ for kpc $\beta=100\ pc$, r — the distance of the star from the Sun, and b — the galactic latitude of the star [13].

The calculation was made under two alternative assumptions $R_0=100$ and 150 pc (in accordance with H. Schmidt and P. B. Shatsova [3], [4]).

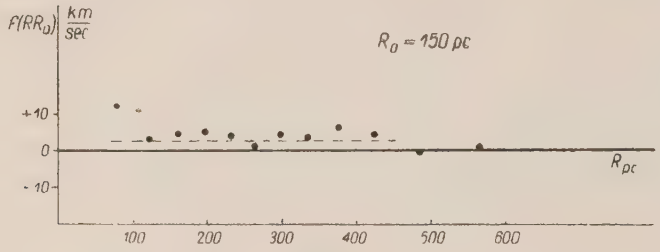

Fig. 1

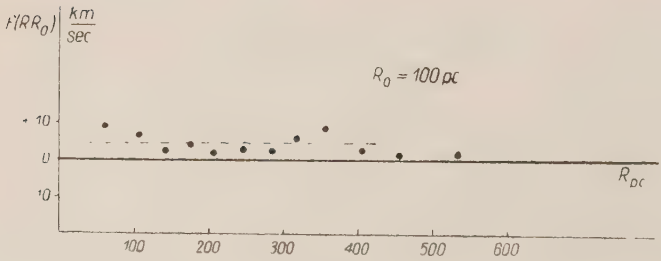

Fig. 2

We thus obtain the two sets of mean $f(RR_0)$ values shown in Fig. 1 and 2, which form lines practically parallel to the R-axis; this means that the rotation of the Local System resembles that of a rigid body.

If we assume that the Sun does not belong to the Local System, and that $\omega(R_0)=0$, we may express the linear velocities V of members of the

System as

$$V = \frac{f(RR_0)}{R_0} R + k.$$

This relation is linear (Figs. 3 and 4). From the least squares solution we obtain:

for $R_0 = 100\ pc$ $V = +0.045\ R - 0.296$ km./sec.,
$\mp 0.021 \quad \mp 5.240$

for $R_0 = 150\ pc$ $V = +0.026\ R + 0.600$ km./sec.,
$\mp 0.011 \quad \mp 2.855.$

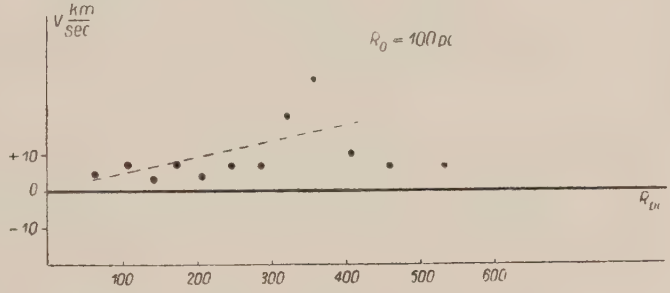

Fig. 3

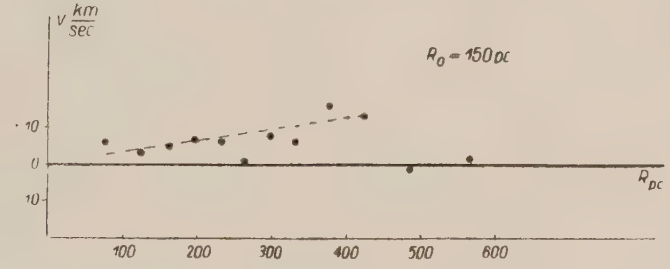

Fig. 4

Thus, the angular velocity of the Local System amounts to:

$$\omega_{100} = 0''.0095 \mp 0''.0044, \quad \omega_{150} = 0''.0055 \mp 0''.0023$$

per annum, and the corresponding periods of rotation are:

$$P = (1.4 \mp 0.6)10^8, \quad P = (2.4 \mp 0.9)10^8 \text{ years.}$$

The results obtained here confirm the general conclusions drawn by P. B. Shatsova and H. Schmidt, though the numerical values differ somewhat from those obtained by those authors. From the results of these authors, we can obtain the following:

P. B. Shatsova	H. Schmidt
$\omega = 0''.0168$ per an.	$\omega = 0''.0076$ to $0''.0110$ per an.
$\omega = 0.8 \cdot 10^8$ years	$P = 1.7 \cdot 10^8$ to $1.2 \cdot 10^8$ years

P. B. Shatsova for R_0 assumes 150 *pc*, and H. Schmidt - - 100 *pc*.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
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ASTRONOMY

On the Rotation of the Local System

by

M. KARPOWICZ

Presented by W. DZIEWULSKI on June 26, 1956

In their study of radial velocities of early spectral class spectroscopic binaries, W. Zonn and the present author [1] found certain peculiarities which suggest the existence of rotation around the centre of the Local System of the nearest binaries. These peculiarities consist in the systematic shift of the l_0 value in Oort's well known formula from 325° towards smaller values, corresponding to the direction of the centre of the Local System, with decreasing distances of stars and systematic decrease of A values with such decreasing distances.

In order to confirm this suggestion, the present study of radial velocities and proper motion of 72 spectroscopic binaries of classes B0-B9 was undertaken. Stars with $45^0 \leqslant l \leqslant 75^0$ and $225^0 \leqslant l \leqslant 255^0$ and with $|b| \geqslant 25^0$ were rejected.

Under the assumption that the orbits of stars within the Local System are circular, the following relations must be fulfilled [2]:

$$\Delta V_r = R_0[\omega(R) - \omega(R_0)] \sin(l - l_0) \cos b, \tag{1}$$

$$\Delta V_r = R_0[\omega(R) - \omega(R_0)] \cos(l - l_0) - r\omega(R) \cos b, \tag{2}$$

where:

ΔV_r — the radial velocity of a centroid of stars;
ΔV_t — the tangential velocity of a centroid of stars;
R_0 — the distance of the centre of rotation from the Sun;
R — the distance of the centroid of stars from the centre of rotation;
r — the distance of the centroid of stars from the Sun;
$\omega(R)$ — the angular velocity of the centroid of stars;
$\omega(R_0)$ — the angular velocity of the Sun;
l_0 — the galactic longitude of the direction of the centre of rotation;
l, b — the galactic longitude and latitude of centroid of stars.

The Bottlinger formulae may be transformed as follows:

$$f(RR_0)=R_0[\omega(R)-\omega(R_0)]=\frac{\Delta V_r}{\sin(l-l_0)\cos b}, \tag{3}$$

$$f(RR_0)=\frac{4.74\,\Delta\mu_i r}{\left[\dfrac{\cos(l-l_0)}{\cos b}-\dfrac{r}{R_0}\right]\cos b}+\frac{r}{\dfrac{\cos(l-l_0)}{\cos b}-\dfrac{r}{R_0}}\omega(R_0). \tag{4}$$

These equations were formulated by G. L. Camm [3] in his study of galactic rotation. In the present paper, they are used in the first place to study the rotation of the Local System.

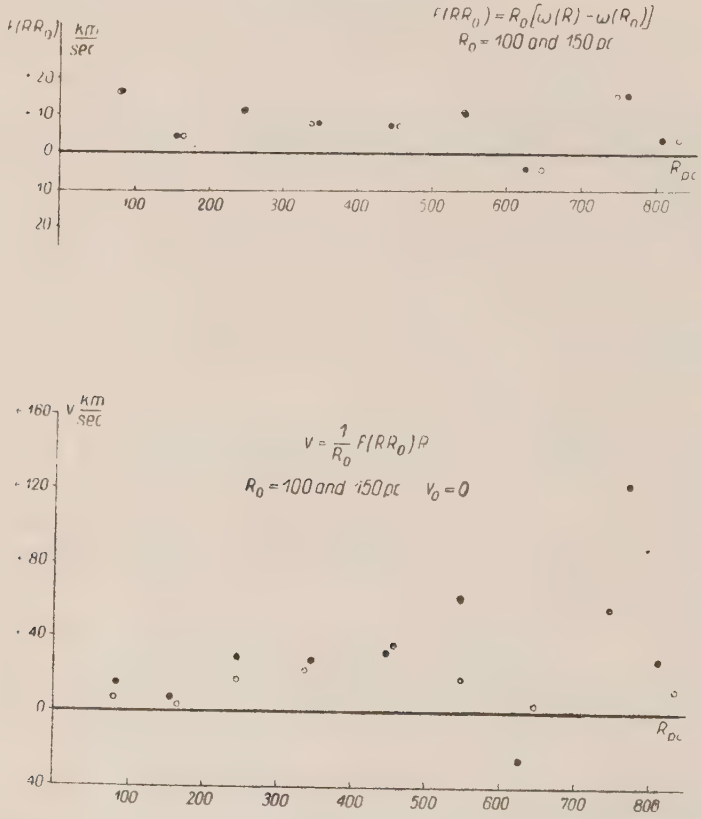

Fig. 1. The dots correspond to $R_0 = 100\ pc$, the circles to $R_0 = 150\ pc$

In both relations, the radial velocities and proper motions must be free from paralactic motion, and from motion around the galactic centre.

In formula (3), all the values on the right are known; for l_0, we put 240° as the longitude of the centre of the Local System.

From the analysis of radial velocities, published by Moore [4], the author obtained the relation $f(RR_0)$; she then drew a diagram in

which the variable R is plotted as an abscissa and $f(RR_0)$ – as an ordinate. In this way, is obtained the line illustrating the character of motion. The mean values obtained, $f(RR_0) = \text{const.}$, suggest that the rotation of the Local System resembles that of a rigid body.

Under the two assumptions, $R_0 = 100$ and $150\ pc$, we obtain:

$$\omega(R) - \omega(R_0) = \begin{cases} 0''.0190 \mp 0''.0061 \text{ per year,} \\ 0''.0148 \mp 0''.0053 \text{ per year.} \end{cases}$$

Taking further different values of $\omega(R_0)$, we obtain different values of $f(RR_0)$ from the relation (4), using all available data for the same objects. The best accord with the results previously mentioned are obtained by $\omega(R_0) = -0''.00588$ per year. Thus we obtain, for angular velocity $\omega(R)$ of the Local System, the following values:

R_0	$\omega(R)$	P
$100\ pc$	$0''.0249 \mp 0''.0061$ per year	$(0.5 \mp 0.2)10^8$ years,
$150\ pc$	$0''.0207 \mp 0''.0053$ per year	$(0.6 \mp 0.3)10^8$ years.

The final column gives the periods of rotation in years.

From the relations (4), we may determine the unknown $\omega(R_0)$ and R_0, if we assume $f(RR_0)$ as determined from radial velocities of stars. Putting $f(RR_0) = L_i$, $\omega(R_0) = x$, $\frac{1}{R_0} = y$, $\frac{L_i}{r}\frac{\cos(l-l_0)}{\cos b} - \frac{4.74\Delta\mu_i}{\cos b} = L_i$, the equations of condition were obtained:

$$x + L_i y = l_i.$$

They were solved by the method of least squares; finally, the following values for unknowns were found:

$$\omega(R_0) = -0''.00168 \mp 0''.00288 \text{ per year,}$$
$$R_0 = 288 \mp 94\ pc,$$

whence

$$V_0 = -2.4 \mp 4.5 \text{ km./sec.}$$

The mean error of $\omega(R_0)$ is considerable, since the motions of stars show considerable dispersions, and the measurements of proper motions are at present too inaccurate to be of much use.

Conclusions

1. The spectroscopic binaries of class B0-B9 take part in the rotation of the Local System. The present results show that the rotation is of a rigid body up to the distance $R < 500\ pc$ from the centre.

2. The velocity of the Sun in relation to the centre of the Local System is close to zero.

3. The distance of the Sun from the centre of the Local System is about 290 *pc*.

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BULLETIN DE L'ACADÉMIE
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A Note on Nuclear Isomerism

by

P. ZIELIŃSKI

Presented by L. INFELD on May 11, 1956

In considering transitions in isomerical nuclei, it may be useful to take into account certain generally neglected effects, which, although usually weak, are, however, of a nature to play a part in certain cases, especially when the usual transition mechanism leads to long lifetimes.

Second-order processes are of this type of effects.

Sachs [1] called attention to the fact that in the case of the transition $J=0\to 0$, *yes*, second-order processes, and more particularly two-quantum emission, might thus come to be of importance, as a result of the selection

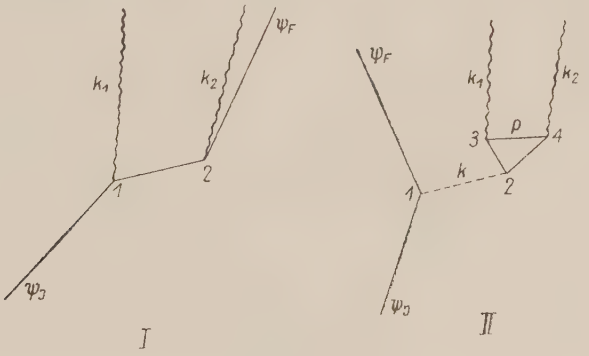

Fig. 1

rules. This conclusion should be subject to experimental verification — the γ-spectrum would in this case be continuous. Further information could be obtained through investigation of angle correlations of emitted photons as considered by Królikowski [2]. As yet no illustrative example has shown up; however, the great stress laid on isomerism makes it possible that this effect may be found.

The present note is concerned with the effect of the meson field in intermediate states on transitions in isomerism in the case of the transition $J=0\to 0$, *yes*, with a transition mechanism alternative to that given by Sachs. Both mechanisms are shown in the respective graphs in Fig. 1.

The meson field intervenes in the mechanism under consideration: the nuclear nucleon emits a virtual π^0-meson, which, by means of a proton-antiproton pair annihilation, decays into two photons. The calculation is to serve as an example and does not give the general solution of the problem; it is, for instance, possible to construct various graphs with charged pions in intermediate states.

The calculation is for weak coupling approximation, applying Feynman's perturbation method. The meson field is $PS(PS)$.

The matrix element of the transition, on taking into account the law of conservation of momentum, may be written as follows (the notation will be immediately clear from Fig. 1, the units system being $\hbar = c = 1$ and that of Heavyside):

$$M_{F\leftarrow I} = -\frac{g^2 e^2}{(2\pi)^2} I_1 \frac{1}{(k_1+k_2)^2-\varkappa^2} \int d_4 p \ \mathrm{Tr}\left[\frac{i\gamma(p-k_2)-m}{(p-k_2)^2+m^2}\gamma \frac{e_2}{\sqrt{2\omega_2}} \frac{i\gamma p - m}{p^2+m^2} \times \right. \tag{1}$$
$$\left. \times \gamma \frac{e_1}{\sqrt{2\omega_1}} \frac{i\gamma(p+k_1)-m}{(p+k_1)^2+m^2}\gamma_5\right],$$

where I_1 denotes the nuclear matrix element

$$I_1 = \int \bar{\psi}_F(x_1)\, e^{-i(k_1+k_2)x_1} \gamma_5 \psi_I(x_1)\, d_4 x_1. \tag{2}$$

After calculating the trace in (1), the following *convergent* integral remains to be computed:

$$\int d_4 p\, [(p-k_2)^2+m^2]^{-1} \cdot [p^2+m^2]^{-1} \cdot [(p+k_1)^2+m^2]^{-1}. \tag{3}$$

The computation of the integral, in a manner analogous to that of Steinberger [3] for the decay of a real π^0-meson into two photons, is restricted to the first term of the expansion in the ratio $\varkappa/m$ of the masses of the meson and nucleon.

The lifetime is obtained in the following form:

$$\tau^{-1} = \frac{1}{210 \cdot (2\pi)^5} \frac{g^4 e^4}{\varkappa^6} \left(\frac{\varkappa}{m}\right)^2 (\Delta E)^7 |I_2|^2. \tag{4}$$

Here ΔE denotes the difference in the initial and final energies of the nucleus, and

$$I_2 = \int \bar{\psi}_F(\vec{x})\, \gamma_5\, e^{-i(\vec{k}_1+\vec{k}_2)\vec{x}}\, \psi_I(\vec{x})\, d_3\vec{x} \tag{5}$$

is the nuclear matrix element.

The angular correlation is approximately determined by the factor

$$w(\theta) \approx (1-\cos\theta)^2, \tag{6}$$

which is proportional to the probability density of the angle between the photons.

In order to estimate roughly the magnitude of this effect, let us assume

$$(7)\quad |I_2| = \left|\int \bar{\psi}_F \gamma_5 e^{-i(\vec{k}_1+\vec{k}_2)\vec{x}} \psi_I d_3\vec{x}\right| \approx \left|\int \bar{\psi}_F \gamma_5 \psi_I d_3\vec{x}\right| \approx \left(\frac{v}{c}\right)^2; \quad \Delta E = 1 \text{ MeV}; \quad \frac{g^2}{4\pi} = 1.$$

This results in a lifetime of the order of $\tau \approx 10^3$ sec.

On comparing this result with the estimate for the alternative process [1], [2], the result is obtained indicating that the process under consideration is the less probable by several orders of magnitudes. However, there is an uncertainty in the comparison. Once the isomer of type $J = 0 \to 0$, *yes*, is discovered, it should be possible to decide, on experimental evidence, whether there is any deviation from the former type of process, by investigating the energy distribution and angular correlations.

The author wishes to express his thanks to J. Dąbrowski for suggesting the idea of the present paper and for numerous discussions, and to W. Królikowski for his valuable remarks.

The author is greatly indebted to Professor L. Infeld and Professor W. Rubinowicz for their kind interest.

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BULLETIN DE L'ACADÉMIE
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CHEMISTRY

On a New Colour Reaction of Aldehydes

by

T. URBAŃSKI

Communicated at the meeting of May 18, 1956

It has been found that diluted aqueous solutions of aldehydes give a *yellow colour* with a solution of 1-amino-8-naphthol-3,6-disulphonic acid (H-acid) or its sodium salt in sulphuric acid (80%).

This appears to be a general reaction of aldehydes.

Preparation of the reagent

A solution of 0.5% H-acid in 80% sulphuric acid was prepared in the following way:

100 ml. sulphuric acid (1.84) were mixed with 33.3 ml. water, and 0.70 g. H-acid were added to obtain a clear solution.

The test

To a few mls. of the reagent c. one ml. of the examined solution was added and then all was shaken. When a solution of high concentration of aldehyde was used, a yellow or orange colour developed immediately. At lower concentrations the colour appeared after warming on a steam-bath for a few minutes.

Sensitivity

The sensitivity of the test can be seen from the lowest concentrations detectable by this method.

The concentrations are tabulated below:

Aldehyde	Detectable concentration per cent
Formaldehyde	0.01
Benzaldehyde	0.01
Cynnamic aldehyde	0.002
Furfural	0.002

Acetaldehyde and homologous aliphatic aldehydes, paraldehyde and various derivatives of benzaldehyde, all give the same colour reaction with H-acid.

Ketones also give a similar reaction, but the sensitivity of the test is much lower. Thus, acetone gives a yellow colour when present in a concentration of 5% or higher.

Experiments on the possibility of using this method for the quantitative determination of aldehydes are now being carried on.

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BULLETIN DE L'ACADÉMIE
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CHEMISTRY

The Existence of σ- and χ-Phases in Rhenium Alloys

by

J. NIEMIEC and W. TRZEBIATOWSKI

Communicated by W. TRZEBIATOWSKI at the meeting on May 18, 1956

There are many known examples of the tetragonal σ-phases occurring in binary and ternary alloys of transition metals, with manganese or its neighbours as one component. χ-phases of the α-Mn type are somewhat scarcely represented, and only 3 of this kind — $Al_{12}Mg_{17}$ [1], $Mo_{10}Cr_{12}Fe_{36}$ [2] and one not precisely determined, occurring in Cr-Mo-Ni steel [3] — are known. Recently, a new example of this type was identified, occurring in the rhenium-titanium alloys and in the composition represented by $Re_{24}Ti_5$ [4]. Therefore it seemed interesting to seek such phases in other rhenium alloys, this metal being in the VII subgroup homologue with manganese.

The following six rhenium systems were investigated:

Re-Nb, Re-Ta, Re-Cr, Re-Mo, Re-W and Re-Fe.

The alloys were prepared from the purest components, by pressing the metallic powders in the desired proportions, annealing in pure hydrogen stream, or arc-melting in purified argon atmosphere.

The alloys were investigated by powder methods using a standard camera of 114 mm. diameter, CuK_α and CrK_α radiation.

It was found that χ-phases occur in niobium and tantalum alloys. In compositions of 25 at. — % Nb, or 25 at. — % Ta, the lattice dimensions of the regular cells were determined to be 9.67_6 and 9.69_7 Å respectively. Accepting $Re_{22}Nb_7$ as the structural formula, and the same atomic co-ordinates as in α-Mn [5], the positions of niobium and rhenium atoms in the unit cell were controlled by random (I) or ordered (II) arrangements (Table I).

TABLE I

Space group $T_d^3 - I\,\bar{4}\,3\,m$

Complexes	2(a)	8(c)	D_1(24 g)	D_2(24 g)
I (random)	—	—	—	—
II (ordered)	2 Nb	8 Nb	4 Nb, 20 Re	24 Re

Only two interferences ($h^2+k^2+l^2=6$ and 8) showed sufficient difference in intensities calculated for ordered and random distribution of atoms. These two interferences would have intensities close to zero in the case of random distribution. Since both interferences were observed, it may be concluded that the ordered arrangement (II) is acceptable.

In the χ-TaRe phase of identical composition ($Re_{22}Ta_7$), the intensities observed agree well with random and ordered distribution of atoms; small differences in the atomic scattering factors between the two elements make no distinction possible.

The existence of σ-phases was established in the following rhenium alloys: Re-Cr, Re-Mo, Re-W, Re-Fe. With the exception of the iron system, this had already been briefly noted [6].

The composition of the σ-phases and the results of our X-ray analysis are given in Table II.

TABLE II

σ-phases

Composition	Sintering temperature °C.	Time h	Unit cell dimensions Å			Electron vacancies per atom N_v	Electron concentrations per atom N_e
			a	c	c/a		
Cr_2Re_3	1600	8	9.31	4.83	0.519	3.84	6.60
Mo_2Re_3	2000	12	9.57	4.98	0.520	3.84	6.60
W_2Re_3	2000	12	9.59	5.00	0.521	3.84	6.60
Fe_3Re_2	1400	4	9.08	4.72	0.520	2.92	7.60

Compounds, such as W_2Re_3 [7] and Fe_3Re_2 [8], are known from phase diagrams, but their crystal structure had not been investigated. Recently, other authors have independently identified σ-MoRe and σ-WRe phases, with lattice constants only slightly differing from our data [9].

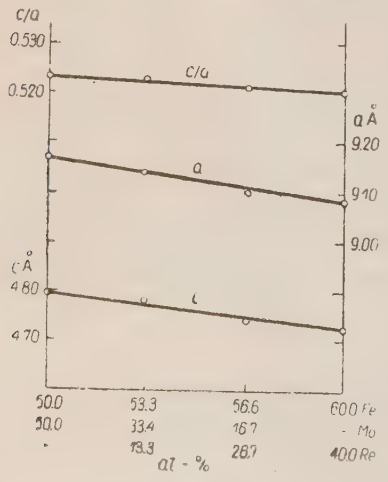

Fig. 1

With a view to confirming the nature of the Fe_3Re_2 phase, mixtures of powdered metals in proportions representing the pseudo-binary section Fe_3Re_2-FeMo of the Fe-Re-Mo system were prepared and sintered at 1400° in hydrogen atmosphere. From powder diagrams it follows that Fe_3Re_2 is isomorphous with FeMo, a typical σ-phase [10]. The lattice parameters vary linearly according to compositions, as shown in Fig. 1.

The existence of σ- and χ-phases has often been related to the electronic structures of the components, expressed by electronic vacancies or concentrations. If the same number, 3.3, of electronic vacancies is assumed in rhenium as in manganese, 4.66 in Cr, Mo and 2.66 in Fe, then the new σ-phases of Cr, Mo and W offer vacancies similar to those in other σ-phases, showing 3.4—3.6 vac./at. [11].

Brillouin polyeders were also constructed for σ-phases. The smaller one gave an electronic concentration of 1.72 el./at. [12]. The second, formed by following the planes: 720, 550, 721, 551, 602, 532, 413, 333 and 004, offered a capacity of 6.97 el./at. [13]. Using nd and $(n+1)s$ electrons, σ-phases of rhenium with chromium, molybdenum and tungsten showed a content of 6.6 el./at., but Fe_3Re_2 differed as regards both electronic vacancies and concentrations.

Therefore, no satisfactory explanation can, at present, be given for the existence of both σ-phases and χ-phases. These phases, being composed from two transition metals, have a more complicated electronic structure than alloys containing only one transition metal and a second of well-defined electronic structure — e. g., aluminum — which enables their mutual reactions to be predicted.

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CHEMISTRY

Conductance of Mono- and Poly-Crystalline Resorcinol

by

A. GOŁĘBIEWSKI

Presented by M. ŚMIAŁOWSKI on June 11, 1956

Researches on conductance of organic compounds in polycrystalline form have involved already about 50 compounds [1]. As regards monocrystals, however, only measurements relating to naphthalene [2], anthracene [3] and phtalocyanine [4] are known, and the results have not been compared with those obtained from polycrystalline samples. This paper presents the results of measurements made on both mono- and polycrystalline resorcinol. Comparison of relevant results shows that conductance depends in this case on the crystalline modification and on the mono- or poly-crystalline form of the sample.

1. Properties of resorcinol and preparation of sample

Resorcinol crystallizes in 2 forms: α and β, the transition point being at 70.8—74° C. According to Robertson and Ubbelohde [5], both modifications have the rhombo-pyramidal structure C_{2v}^{9}-Pna, both are colourless and enantiotropic. The lower-temperature modification α has a lesser density resulting from the stiffening effect of hydrogen bonds in this modification. As the temperature rises, the stiffening effect decreases, making possible conversion into another crystalline modification. The absorption spectrum of the modification α reveals a band with a threshold 4.29 eV [6] on the long-wave side.

Resorcinol was purified by 3 to 5-fold sublimation or by vaporisation *in vacuo* at a temperature of 100—130° C. in semi-darkness. As regards polycrystalline samples, the last sublimate α and β crystals were separated by visual selection. They were ground and pressed in tablet form, 4.5—5.5 mm. in diametr and 3.5—4.5 mm. thick. Points of contact with electrodes were coated with coloidal graphite. Conductance was measured by methods used by K. Pigoń as regards hydroquinone [7]. The readings

were taken in hydrogen after some 10—20 hours of heating in diffusion vacuum, or, occasionally, directly in hydrogen.

Monocrystals were obtained by the Mette and Pick method [3] adapted to resorcinol. The resulting crystals were of the modification β. Cubes $4 \times 4 \times 4$ mm. were split from the monocrystals, coated on two sides with coloidal graphite, and readings were taken analogically as in the case of polycrystalline samples.

2. Results of measurements on polycrystalline samples

Activation energy, conductivity σ_{15} (at 15° C.), in ohm.$^{-1}$ cm.$^{-1}$ and the values of σ_0 were determined graphically on the basis of the formula $\sigma = \sigma_0 \cdot e^{-E/2kT}$. Within 30—94° C. both modifications showed two mechanisms of conductance, with an abrupt transition taking place at about 63° C. average. This corresponds more or less to the transition temperature of both modifications, particularly since the method used permitted absolute temperatures to be read only to an accuracy of several degrees, with a systematic error towards lower temperatures. A similar change in the vicinity of phase conversion (130° C.) was observed by Pigoń in the related hydroquinone.

Irrespective of the modification, α or β, used for measurements, a sample heated for a sufficiently long time, at a temperature below 63° C. yielded, below this temperature, reproducible values of activation energy $E = 2.10$ eV, conductivity $\sigma_{15} = 0.5 \cdot 10^{-16}$, $\sigma_0 = 2 \cdot 10^2$, and irreproducible values above this temperature of activation energy 2.60—3.18 eV. Similarly, irrespective of the modification used for measurements, a sample heated for an sufficiently long time at a temperature above 63° C. showed irreproducibility of results below this temperature of $E = 2.13 - 2.70$ eV, and reproducibility of results above 63° C. of $E = 3.27$ eV, $\sigma_{15} = 0.5 \cdot 10^{-18}$, $\sigma_0 = 2 \cdot 10^{11}$. This may be explained by slow and gradual conversion of one modification into the other.

3. Results of measurements on monocrystals

Conductance of monocrystals of resorcinol β was measured within the range of temperatures of 56—98° C. Only one mechanism of conductance was established within the range referred to. Taking into account the experimental error, no differences were established as between readings obtained at various positions of the crystal in relation to electrodes. The mean values read were: $E = 4.24$ eV, $\sigma_{15} = 2 \cdot 10^{-19}$, $\sigma_0 = 5 \cdot 10^{18}$. Clouding of the monocrystalline sample induced suppression of conductance of $E = 4.24$ eV, and appearance of conductance of $E = 3.27$ eV — that is of the same activation energy as in polycrystalline β resorcinol.

4. Discussion

In organic semi-conductors, there is frequently observed a concordance of thermal and optical activation energy (naphtalene [2], anthracene [4], [8], hydroquinone [7]). Such concordance exists also, in the case of resorcinol monocrystals, for the optical threshold 4.29 eV and thermal activation energy 4.24 eV. Consequently, the mechanism corresponding to this activation energy is likely to be electronic. The high value $\sigma_0 = 10^{18}$ of this mechanism is worthy of note.

Conductivity of the same modification in polycrystalline state of $E = 3.27$ eV is probably the resultant of conductance of $E = 2.1$ eV, and electronic conductance of $E = 4.2$ eV. This is borne out by a simple calculation. Let us find such x and y as to express the curve corresponding to the conductance of $E = 3.27$ eV most exactly, as the sum of conductances:

$$\sigma_0(E=3.27)\cdot e^{-\frac{3.27}{2kT}} = x\cdot e^{-\frac{2.10}{2kT}} + y\cdot e^{-\frac{4.24}{2kT}}.$$

Determining the unknown x and y from data corresponding to the mean transition point of 63° C., and from data corresponding to the temperature of 90° C., we obtain

$$x = 2.8\cdot 10^2; \qquad y = 1.1\cdot 10^{18}.$$

Agreement of these figures with the readings $2\cdot 10^2$ and $5\cdot 10^{18}$ is satisfactory.

It is not impossible, however, that this agreement may be accidental, and that conductance of $E = 3.27$ eV represents conductance in the pure sense, e. g., of the ionic type. Considerations on the structure of both modifications lead to the conclusion that ionic conductance is possible in the modification β, particularly owing to the notable resistance to electronic conductivity of resorcinol.

It also follows from these considerations that ionic conductivity is considerably less likely in the modification α. Consequently, the conductivity of $E = 2.10$ eV in the polycrystalline modification α, is likely to correspond to the electronic mechanism. Analogy between the optical spectra of benzene and of mono- and di-substituted benzene derivatives makes it possible to assume that there also exists in the case of resorcinol an extremely weak optical transition with a maximum at about 2.3 eV, and a threshold about 2,1—2.2 eV.

The weak sensitivity of conductances to the mode of sample preparation tends to indicate that all three conductances are spontaneous.

A complete description of experiments and of results of measurements, together with a more detailed discussion will be published in Annals of Chemistry (Roczniki Chemii).

I am deeply indebted to Professor K. Gumiński for the great interest he took in this work, and to K. Pigoń, both for kindly permitting me to carry out measurements at the Chair of Physical Chemistry in the Wrocław Technological Institute, and for his highly valuable advice and discussions.

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CHEMISTRY

Boiling Temperature of Positive Ternary Azeotropes. II

by

W. MALESIŃSKI

Presented by W. ŚWIĘTOSŁAWSKI on June 21, 1956

1. Introductory remarks

Previously [1], we derived a simple relation between the boiling temperature of a positive ternary azeotrope and the boiling temperature of positive binary azeotropes formed by components 1, 2 and 3 of this system. The equation has the form:

$$\delta_{123} = \delta_{12} + \delta_{23}, \tag{1}$$

in which δ are the respective azeotropic depressions: $\delta_{123} = T_2 - T_{Az}^{(123)}$, $\delta_{12} = T_2 - T_{Az}^{(12)}$, and $\delta_{23} = T_2 - T_{Az}^{(23)}$; $T_{Az}^{(123)}$, $T_{Az}^{(12)}$, $T_{Az}^{(23)}$ being the boiling temperatures of azeotropes 1,2,3; 1,2 and 2,3 at the constant pressure considered.

In deriving this relation, we have assumed a) that the solutions are regular, and b) that the constants, appearing in the equations determining the activity coefficients of these solutions are correlated by an equation previously given [2]. The latter was derived on the basis of the scheme of formation of azeotropes given by Świętosławski [3]. The assumption b) restricts our considerations to mixtures of molecules in which no specific interaction takes place. It should be emphasised that the relation referred to between regular solution constants leads to certain new relations, differing from Haase's [4] general considerations relating to the azeotropic systems formed by regular solutions.

Hitherto, we have assumed that the vaporisation entropies of pure components at their boiling temperatures are equal. The relations determining the boiling temperature of a ternary azeotrope will here be considered for the case of different vaporisation entropies of the components. The errors to be expected, when using relation (1) in such cases, will also be taken into consideration.

2. General considerations

Our considerations will be based on the relation, [1]:

$$\Delta S_2 (T_{Az}^{(123)} - T_2) + A_{12} (x_1^{(123)})^2 + A_{23} (x^{(123)})^2 = 0, \tag{2}$$

in which ΔS_2 stands for the vaporisation entropy of component 2 at its boiling temperature, A_{12}, A_{23} – for regular solution constants, and $x_1^{(123)}$, $x_3^{(123)}$ – for mole fractions of components 1 and 3 in the ternary azeotrope. Component 2 is the main azeotropic agent [2], [3].

Equation (2) may be rewritten in the form:

$$\delta_{123} = \frac{A_{12}}{\Delta S_2} \cdot (x_1^{(123)})^2 + \frac{A_{23}}{\Delta S_2} (x_3^{(123)})^2. \tag{3}$$

We now make use of the relation between the composition of a ternary azeotrope and compositions of the binary azeotropes for the case of different vaporisation entropies of the components [5]:

$$x_1^{(123)} = x_1^{(12)} + \Delta x_1, \tag{4a}$$

$$x_3^{(123)} = x_3^{(23)} + \Delta x_3; \tag{4b}$$

$x_1^{(12)}$ and $x_3^{(23)}$ are the mole fractions of components 1 and 3 in binary azeotropes 1,2 and 2,3 and:

$$\Delta x_1 = \frac{(T_{Az}^{(12)} - T_{Az}^{(123)}) \cdot (\Delta S_2 - \Delta S_1)}{2A_{12}}, \tag{5a}$$

$$\Delta x_3 = \frac{(T_{Az}^{(23)} - T_{Az}^{(123)}) \cdot (\Delta S_2 - \Delta S_3)}{2A_{23}}. \tag{5b}$$

Substituting (4a) and (4b) into (3), and taking into account that the azeotropic depressions are related [6] with the compositions by the following equations:

$$\delta_{12} = \frac{A_{12}}{\Delta S_2} (x_1^{(12)})^2, \qquad \delta_{23} = \frac{A_{23}}{\Delta S_2} (x_3^{(23)})^2, \tag{6}$$

we obtain

$$\delta_{123} = \delta_{12} + \delta_{23} + \Delta\delta_{12} + \Delta\delta_{23}. \tag{7}$$

The symbols $\Delta\delta_{12}$ and $\Delta\delta_{23}$ represent the respective temperature corrections associated with the inequality of vaporisation entropies. They are determined as follows:

$$\Delta\delta_{12} = 2\frac{A_{12}}{\Delta S_2} x_1^{(12)} \cdot \Delta x_1 + \frac{A_{12}}{\Delta S_2} (\Delta x_1)^2, \tag{8a}$$

$$\Delta\delta_{23} = 2\frac{A_{23}}{\Delta S_2} x_3^{(23)} \cdot \Delta x_3 + \frac{A_{23}}{\Delta S_2} (\Delta x_3). \tag{8b}$$

Introducing the values of lower portions of the azeotropic ranges $Z_{d_{21}}$ and $Z_{d_{23}}$ which are defined as (6),

$$Z_{d_{21}} = \frac{A_{12}}{\Delta S_2} \quad \text{and} \quad Z_{d_{23}} = \frac{A_{23}}{\Delta S_2}, \tag{9}$$

we arrive at the equations:

(10a) $$\Delta\delta_{12}=2Z_{d_{21}}x_1^{(12)}\cdot\Delta x_1+Z_{d_{21}}(\Delta x_1)^2,$$

(10b) $$\Delta\delta_{23}=2Z_{d_{23}}x_3^{(23)}\cdot\Delta x_3+Z_{d_{23}}(\Delta x_3)^2.$$

The correction values of azeotropic depressions $\Delta\delta_{12}$ and $\Delta\delta_{23}$ may be correlated also with temperature parameters. Eliminating from (10a) and (10b) the values $x_1^{(12)}$ and $x_3^{(23)}$ (in accordance with (6a) and (6b)), and the values Δx_1 and Δx_3 by means of equations (5a) and (5b), and introducing as constants the values of lower portions of the azeotropic ranges, we obtain the equations:

(11a) $$\Delta\delta_{12}=\sqrt{\frac{\delta_{12}}{Z_{d_{21}}}}(T_{Az}^{(12)}-T_{Az}^{(123)})\left(1-\frac{\Delta S_1}{\Delta S_2}\right)+\frac{1}{4Z_{d_{21}}}\left[(T_{Az}^{(12)}-T_{Az}^{(123)})\left(1-\frac{\Delta S_1}{\Delta S_2}\right)\right]^2,$$

(11b) $$\Delta\delta_{23}=\sqrt{\frac{\delta_{23}}{Z_{d_{23}}}}(T_{Az}^{(23)}-T_{Az}^{(123)})\left(1-\frac{\Delta S_3}{\Delta S_2}\right)+\frac{1}{4Z_{d_{23}}}\left[(T_{Az}^{(23)}-T_{Az}^{(123)})\left(1-\frac{\Delta S_3}{\Delta S_2}\right)\right]^2.$$

If the vaporisation entropies are equal ($\Delta S_1=\Delta S_2$ and $\Delta S_3=\Delta S_2$), then $\Delta\delta_{12}$ and $\Delta\delta_{23}$-values become equal to zero, i. e., relation (7) becomes identical with (1). If the vaporisation entropies are different, the sign of the temperature corrections $\Delta\delta_{12}$ and $\Delta\delta_{23}$ depends on the values of their respective ratios. If the ratios $\Delta S_1/\Delta S_2$ and $\Delta S_3/\Delta S_2$ are less than unity, then $\Delta\delta_{12}$ and $\Delta\delta_{23}$ are positive. If, however, these ratios are greater than unity, the first terms of equations (11) become negative; the remainder are always positive. Consequently, the sign of temperature corrections depends on the absolute value of the terms.

3. Approximate values of the temperature corrections for azeotropic depressions

The terms Δx_1 and Δx_3, correcting the composition of the ternary azeotrope in the case of different vaporisation entropies of the components, have been previously discussed [5]. The conclusion was drawn that they are in general of the order of several mole percent. Therefore, the second terms in (10) and (11) may be omitted, but this simplification is admissible only if the absolute values of Δx_1 and Δx_3 are much smaller than $x_1^{(123)}$ and $x_3^{(123)}$, because only then are the second terms very small compared with the first. Thus we have:

(12a) $$\Delta\delta_{12}=2Z_{d_{21}}x_1^{(12)}\Delta x_1,$$

(12b) $$\Delta\delta_{23}=2Z_{d_{23}}$$ [illegible]

and

(13a) $$\Delta\delta_{12}=\sqrt{\frac{\delta_{12}}{Z_{d_{21}}}}(T_{Az}^{(12)}$$ [illegible] $$-\frac{\Delta S_1}{\Delta S_2}\Big),$$

(13b) $$\Delta\delta_{23}=\sqrt{\frac{\delta_{23}}{Z_{d_{23}}}}(T_{Az}^{(23)}$$ [illegible] $$-\frac{\Delta S_3}{\Delta S_2}\Big).$$

These relations may be further transformed in different ways. First of all may be expressed the dependence of the corrections for azeotropic depressions $\Delta\delta_{12}$ and $\Delta\delta_{23}$ on the depressions themselves. To do this, we make use of equation (1) in the form:

(14a) $$T_{Az}^{(12)} - T_{Az}^{(123)} = \delta_{23},$$

(14b) $$T_{Az}^{(23)} - T_{Az}^{(123)} = \delta_{12}.$$

Substituting the above equations into equations (13a) and (13b), we obtain:

(15a) $$\Delta\delta_{12} = \sqrt{\frac{\delta_{12}}{Z_{d_{21}}}\,\delta_{23}} \cdot \left(1 - \frac{\Delta S_1}{\Delta S_2}\right),$$

(15b) $$\Delta\delta_{23} = \sqrt{\frac{\delta_{23}}{Z_{d_{23}}}\,\delta_{12}} \cdot \left(1 - \frac{\Delta S_3}{\Delta S_2}\right).$$

In addition, taking into consideration the relations (5):

(16a) $$\Delta x_1 = \frac{\delta_{23}}{2Z_{d_2}} \cdot \left(1 - \frac{\Delta S_1}{\Delta S_2}\right),$$

(16b) $$\Delta x_3 = \frac{\delta_{12}}{2Z_{d_{23}}} \cdot \left(1 - \frac{\Delta S_3}{\Delta S_2}\right),$$

and substituting in (12a) and (12b) values Δx_1 and Δx_3 expressed in that way, we obtain the relations between the corrections and the azeotropic depression and composition:

(17a) $$\Delta\delta_{12} = x_1^{(12)} \cdot \delta_{23}\left(1 - \frac{\Delta S_1}{\Delta S_2}\right),$$

(17b) $$\Delta\delta_{23} = x_3^{(23)} \cdot \delta_{12}\left(1 - \frac{\Delta S_3}{\Delta S_2}\right).$$

With the aid of these relations, the magnitude of $\Delta\delta_{12}$ and $\Delta\delta_{23}$ may be roughly estimated. Substitution of numerical values indicates that the temperature corrections vary mostly within the limits of several tenths of a degree, sometimes reaching several degrees.

The possibility of a compensation of the deviations should be taken into account. The final correction for boiling temperature of a ternary azeotrope depends on the $(\Delta\delta_{12}+\Delta\delta_{23})$ value. If $\Delta S_1 > \Delta S_2 > \Delta S_3$ or $\Delta S_1 < \Delta S_2 < \Delta S_3$, then $\Delta\delta_{12}$ and $\Delta\delta_{23}$ have opposite signs and to some extent compensate one another. Bearing in mind that component 2 is characterised by the medium value of internal pressure, we may conclude that such compensation is likely to occur very frequently. This results from the fact that the vaporisation entropy increases in most cases with the internal pressure, and then the above inequalities are fulfilled.

Summary

The equations previously derived for the boiling temperature of positive ternary azeotropes (1) are extended to the cases of unequal vaporisation entropies of the components. This is expressed as follows:

(7) $$\delta_{123} = \delta_{12} + \delta_{23} + \Delta\delta_{12} + \Delta\delta_{23},$$

in which $\delta_{123} = T_2 - T_{Az}^{(123)}$, $\delta_{12} = T_2 - T_{Az}^{(12)}$, $\delta_{23} = T_2 - T_{Az}^{(23)}$. T_2 is the boiling temperature of the main azeotropic agent, and $T_{Az}^{(123)}$, $T_{Az}^{(12)}$, $T_{Az}^{(23)}$ the boiling temperatures of the respective azetropes. Symbols $\Delta\delta_{12}$ and $\Delta\delta_{23}$ are the temperature corrections resulting from inequality of vaporisation entropies. In most cases, $\Delta\delta_{12}$ and $\Delta\delta_{23}$ have opposite signs, so that some compensation takes place, producing a decrease of the correction value.

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CHEMISTRY

Influence of Ion Size on Quantitative Proportions of the Components in Binary salts. IV

by

T. PENKALA

Presented by W. ŚWIĘTOSŁAWSKI on July 5, 1956

According to the previous relation [1] for a series of binary systems of inorganic compounds, as the difference of the ionic sizes of salts increases, the systems change gradually from a solid solution, through solid solutions with increasing miscibility gap, to ideal eutetics. These changes are in conformity with Świętosławski's scheme [2] of such series, of systems formed by organic substances. It was also shown that binary salts are formed if the size differences in the ions of both components are sufficiently great. Further investigations based on literature data lead to the conclusion that the quantitative proportion of the components in compounds formed by the two salts depends primarily on the quotient of ion size of these salts.

Binary systems formed by salts possessing identical anions and different cations with the same valency, are characterised by a regularity — that is, the greater the difference in the size of the cations, the greater is the content of the smaller cation in the binary salt. For example, the following binary salts are formed in the series of systems CuCl — chlorides of monovalent metals: $CuCl \cdot 2KCl$ (proportion of the content of smaller cation to the greater is equal to 1/2), $CuCl \cdot 2RbCl$ (1/2), $3CuCl \cdot 2RbCl$ (3/2), $2CuCl \cdot 3CsCl$ (2/3), $2CuCl \cdot CsCl$ (2/1).

Radii of ions forming the systems under consideration are: (in Å units): $Cu^{\cdot}$—0.63; $Li^{\cdot}$—0.78; $Na^{\cdot}$—0.98; $Ag^{\cdot}$—1.13; $K^{\cdot}$—1.33; $Rb^{\cdot}$—1.49; $Cs^{\cdot}$—1.65; $Be^{\cdot\cdot}$—0.34; $Mg^{\cdot\cdot}$—0.78; $Ca^{\cdot\cdot}$—1.06; $Sr^{\cdot\cdot}$—1.27; $Mn^{\cdot\cdot}$—0.91; $Co^{\cdot\cdot}$—0.82; $Tl^{\cdot}$—1.49; OH'—1.53; Cl'—1.81; Br'—1.96; J'—2.20.

Similarly, in binary systems formed by Li_2So_4 with sodium and potassium sulphates, with an increase in the size differences of cations, the increase in content of Li_2SO_4 (smaller cation) in the binary salt is evident, e. g., $Li_2SO_4 \cdot 2Na_2SO_4$ (1/2), $Li_2SO_4 \cdot Na_2SO_4$ (1/1), $Li_2SO_4 \cdot K_2SO_4$

(1/1), $2Li_2SO_4 \cdot K_2SO_4$ (2/1). In systems composed of Li_2MoO_4 and Na_2MoO_4 and K_2MoO_4, the following compounds were found: $Li_2MoO_4 \cdot 3Na_2MoO_4$ (1/3) and $Li_2MoO_4 \cdot K_2MoO_4$ (1/1).

Deviations from this regularity are observed in the case of a very strong ionic polarisation, as for example in systems formed by AgI with KI and RbI, where the following salts are known: $2AgI \cdot KI$ (2/1) and $AgI \cdot 2RbI$ (1/2).

In series of binary systems composed of one compound A with a series $B_1, B_2, B_3, \ldots$ having the same cation as A and different anions, it is probable that an analogous regularity exists, i. e., the greater the size differences in the anions, the higher is the content of the smaller anion in the compound formed. For example, LiOH forms with lithium halogens the following binary salts: $2LiOH \cdot 3LiCl$ (2/3), $3LiOH \cdot LiBr$ (3/1), $3LiOH \cdot LiI$ (4/1).

Similar behaviour may be observed in a series of binary systems formed by salts A, composed only of monovalent ions with salts of the series $B_1, B_2, B_3, \ldots$ having the same anion and bivalent cations. In this case, if the monovalent cation of A is sufficiently large, then the smaller the bivalent cation of salt B, the higher is the content of the bivalent cation in the binary salt. The following examples may be given: $CaCl_2 \cdot TlCl$ (1/1), $2MgCl_2 \cdot TlCl$ (2/1); $BaCl_2 \cdot 2RbCl$ (1/2), and $SrCl_2 \cdot RbCl$ (1/1).

In series of binary systems formed by salt A, possessing a relatively small bivalent cation, with the salts of the series $B_1, B_2, B_3, \ldots$ with the same anion as in A, and different monovalent cations, it may be observed as a regularity that the greater the monovalent cation, the higher the content of the binary cation in the binary salt, i. e., the mole quotient A/B increases. For instance, in systems $CaSO_4$–Na_2SO_4 and $CaSO_4$–K_2SO_4, the following binary salts are formed: $CaSO_4 \cdot 3Na_2SO_4$ (1/3), and $2CaSO_4 \cdot K_2SO_4$ (2/1). In system $MnSO_4$–Na_2SO_4, there exist salts of type AB_3 (1/3) and A_3B_2 (3/2), and in system $MnSO_4$–K_2SO_4 – the salt $2MnSO_4 \cdot K_2SO_4$ (2/1). The system $CoSO_4$ with Na_2SO_4 forms the salt AB_3 (1/3), and $CoSO_4$ with K_2SO_4 – the salts AB (1/1) and A_2B (2/1).

Summary

Świętosławski's scheme [2] consisting in a gradual transition from binary solid solutions, through solid solutions with miscibility gap, to ideal eutectics, was extended to inorganic salts by considering the case of great differences in the size of the ions involved. In such a case, binary salts are formed, and the mole quotient of the components depends on the ion sizes. In binary salts formed by components having identical anions and different cations of the same valency, the content of the smaller cation increases with increasing size differences of the cations.

In binary salts formed by compounds with identical anions and cations of different valency (mono- and bi-), the higher the content of the bivalent cation observed, the smaller this cation, and the larger the monovalent cation.

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CHEMISTRY

Gradual Transition in Series of Binary Systems from Compounds Melting Incongruently to Congruently. V

by

T. PENKALA

Presented by W. ŚWIĘTOSŁAWSKI on July 5, 1956

It was stated previously [1] that in a series of binary systems formed by inorganic salts there exists a regularity, so that binary salts are formed if the ions of the components differ sufficiently in size from one another. Investigations, based on literature data, indicate that in systems composed of the salt A with a salt of the series, $B_1, B_2, B_3, \ldots$ with the same anion and different cations of equal valency, there takes place with increasing size difference of the cations, a transition to other compound types, or a gradual transition from compounds melting incongruently to those of the same type melting congruently (Fig. 1).

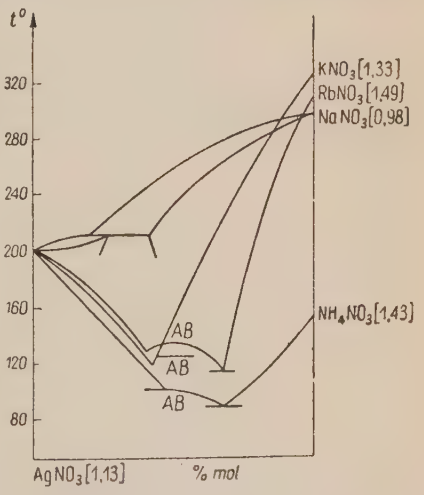

Fig. 1. Series of binary systems formed by $AgNO_3$ with $NaNO_3$, KNO_3, NH_4NO_3 and $RbNO_3$. With the increase in size differences of the cation, a gradual transition occurs from compounds of type AB melting incongruently to those of the same type melting congruently. (In brackets, ionic radii in Å units).

Similar regularity exists in series of binary systems composed of a salt A with monovalent ions and the salts of the series $B_1, B_2, B_3, \ldots$ characterised by the same anion and bivalent cations. If the monovalent cation is sufficiently large, then the smaller the bivalent cation, the more probable is the formation of a compound melting congruently. (Fig. 2).

Fig. 2 shows that with a decrease in the size of the bivalent cation, there exists at first a transition from a compound of type AB, melting incongruently, to compounds of the same type melting congruently, and then

to another type AB_2, with a higher content of bivalent ion, melting incongruently.

In a series of binary systems formed by salt A, having a relatively small bivalent ion, with the salt of the series $B_1, B_2, B_3, \ldots$ having the same anion as A, but monovalent cations, the following regularity is observed:

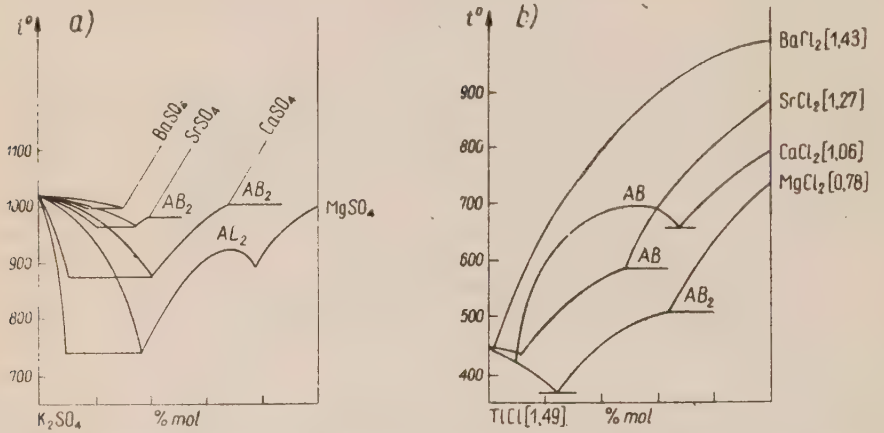

Fig. 2. Gradual transition from incongruently melting compounds to compounds melting congruently in a series of binary systems composed of salts with monovalent ions and salts with bivalent cations.

the larger the monovalent cation, the more probable is the transition from a compound melting incongruently to one of the same type melting congruently. (Fig. 3).

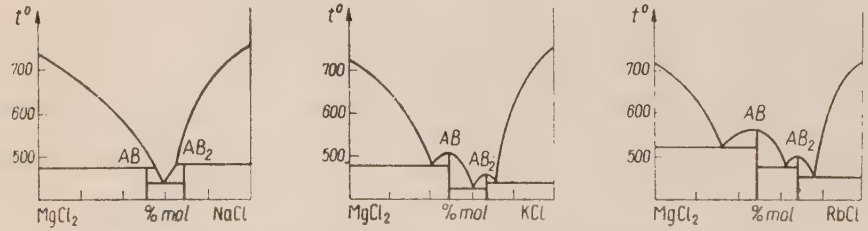

Fig. 3. Transition from binary salts melting incongruently to salts melting congruently in systems formed by a salt of a bivalent metal with the salts having monovalent cations.

In the system MgF_2—KF, there exists a binary salt AB melting congruently, and AB_2 melting incongruently. On the other hand, in system MgF_2-RbF, both the salts (AB and AB_2) melt congruently. The system BeF_2-LiF is characterised by two binary salts of type AB and AB_2 melting incongruently; the system BeF_2-NaF, however, is characterised by salts of the same type melting congruently. Fig. 3 represents an analogous behaviour of systems formed by $MgCl_2$ with NaCl, KCl and RbCl. The binary salts of the system $MgCl_2$—NaCl belong to the type AB and AB_2,

and melt incongruently, whereas in systems with larger monovalent cations, i. e., $MgCl_2$—KCl and $MgCl_2$—RbCl, salts of the same type melt congruently.

Summary

A gradual transition from compounds melting incongruently to those melting congruently is shown in a series of binary systems formed by salt A with those of the series $B_1, B_2, B_3, \ldots$ containing the same anion. If salt A and salts $B_1, B_2, B_3, \ldots$ have cations of equal valency, the transition occurs gradually with increasing size differences in the cations. If salt A contains a large monovalent cation, and salts of the series $B_1, B_2, B_3, \ldots$ – bivalent cations, then, as the size of the bivalent cation decreases, there may be observed a transition from compounds melting incongruently to those melting congruently. If salt A contains a small bivalent cation, and those belonging to series B — monovalent ones, the same transition is associated with an increase in the size of the monovalent cation.

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CHEMISTRY

Binary Azeotropes Formed by Propionic Acid with the Series of *n*-Paraffins

by

W. TRĄBCZYŃSKI

Presented by W. ŚWIĘTOSŁAWSKI on July 5, 1956

Introductory remarks

The purpose of the present paper is to determine the boiling temperatures and the compositions of binary azeotropes formed by propionic acid with the series of normal paraffins. The data available in literature [1], [2] for these systems are incomplete and seem to be doubtful, since they were obtained by fractional distillation. The use of this method may lead to serious errors in the determination of azeotropic parameters, due to insufficient fractional distillation and, in general, to the asymmetry of the boiling temperature isobars in relation to the tangent line drawn through the azeotropic point [3]. In particular, the azeotropic composition may be erroneously determined if the isobars are very flat at the vicinity of the azeotropic point. These errors are almost eliminated if the ebulliometric method is used [4], since it makes it possible to estimate not only the azeotropic parameters, but also the total boiling temperature isobars.

Recently, an analogous series of systems was investigated by Kurtyka [5]. Acetic acid and *n*-paraffins were the subject of the investigation.

Experimental results

The experiments were carried out using two Świętosławski ebulliometers. In the three-stage ebulliometer, the changes in boiling temperature were measured in the course of successive additions of known amounts of one of the components. The simple ebulliometer, filled with water, was used for recording small atmospheric pressure changes. The thermometers were calibrated by comparison with the platinum resistance thermometer.

Five isobars, shown in Fig. 1, were obtained for mixtures of propionic acid with the *n*-aliphatic hydrocarbons ranging from *n*-heptane to *n*-undecane. The numerical results are collected in the table herewith. In column II of this table are given the boiling temperatures of the components; in column III — those of the binary azeotropes formed by propionic acid with the relative hydrocarbon. The azeotropic depressions, the azeotropic compositions by weight and by mole percentages of propionic acid, are listed in columns IV, V, and VI, respectively.

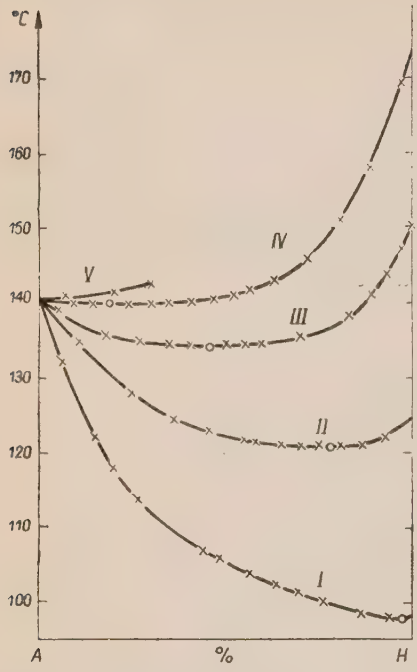

Fig. 1. Boiling temperature isobars of binary mixtures of propionic acid (*A*) with normal paraffins (*H*), ranging from *n*-heptane (I) to *n*-undecane (V). Compositions expressed in weight per cent. The azeotropic points are shown as circles.

The results obtained indicate that in systems of propionic acid with *n*-heptane, *n*-octane, *n*-nonane and *n*-decane, positive azeotropes are formed. The first of these is characterised by an almost tangent azeotrope (azeotropic depression = 0.33° C), and therefore may be considered as approximately limiting the lower portion of the azeotropic range. The system with *n*-nonane shows the greatest depression, 6.78°. The upper portion of this azeotropic range could not be determined directly because the investigated part of the isobar (system with *n*-undecane) does not possess any minimum. On the other hand, the isobar of propionic acid with *n*-decane is not tangent, since the azeotropic depression is equal to 1.29° C.

TABLE

I	II	III	IV	V	VI
Propionic acid	141.05	—	—	100	100
n-Heptane	98.15	97.82	0.33	2	2.7
n-Octane	125.12	120.89	4.23	21.5	29.7
n-Nonane	150.67	134.27	6.78	54	67
n-Decane	174.06	139.76	1.29	80.5	88.8
n-Undecane	193.85	—	—	0	0

All the isobars are very flat and asymmetrical. From this point of view they are similar to those investigated by Kurtyka [5]. These facts

should be considered when choosing the method of determining the azeotropic parameters of such systems. It is believed that the ebulliometric method is to some extent advantageous in these cases.

Summary

The boiling temperature isobars of binary systems of propionic acid (A), with *n*-heptane (I), *n*-octane (II), *n*-nonane (III), *n*-decane (IV) and *n*-undecane (V), were determined by the ebulliometric method. In all the systems, except (V), positive azeotropes are formed, i. e., the respective hydrocarbons lie within the azeotropic range of propionic acid as regards *n*-paraffins. The azeotrope in (I) is almost tangent, and thus system (I) limits the lower portion of the azeotropic range. At the vicinity of the azeotropic point the isobars are asymmetrical and very flat.

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CHEMISTRY

On Fungicide Activities of Some Aryloxyacethydroxamic Acids

by

Z. ECKSTEIN and T. URBAŃSKI

Communicated by T. URBAŃSKI on July 6, 1956

Aryloxyacethydroxamic acids are relatively little known compounds. The properties of phenoxyacethydroxamic acid only have been described [1] in a detailed manner. 2,4-Dichlorophenoxyacethydroxamic acid has been examined [2] as a weed-killing compound (it possesses c. 80% of the activity of 2,4-D), and 1-naphthoxyacethydroxamic acid [3] was found to be tuberculostatic *in vitro*. However, the properties of these two acids have not been mentioned in these publications.

The discovery of the physiological activity of the hydroxamic acid mentioned above appeared to be particularly interesting and led us to prepare and examine a number of aryloxyacethydroxamic acids and their derivatives, particularly from the point of view of their fungistatic activity. There are some data in the literature which indicate the parallelism between antituberculous and fungicide activity of salicylhydroxamic acid [4].

On the other hand, hydroxamic acids readily form chelate compounds with metals such as copper. The statement of their activity could support the hypothesis on the relation between the fungicide activity of some organic compounds and their ability to form chelates with trace metals, important to the normal trend of the enzymatic processes in the living cell of microorganisms.

A number of aryloxyacethydroxamic acids have been prepared by the method consisting in acting with an excess of hydroxylamine and sodium methoxide on methanolic solutions of corresponding ethyl esters of aryloxyacetic acids [5].

The properties of the compounds thus obtained are shown in Table I.

Aryloxyacethydroxamic acids are colourless cristalline substances. Their alcoholic solutions give a colour-reaction with ferric chloride typical for hydroxamic acids. They form green chelate compounds with cupric

salts and can be readily acetylated. Experimental details on the preparation of these compounds will be reported elsewhere [6].

TABLE I

R-O-CH_2-COHNOH

No.	R	M. p. (° C). (with decomp.)	Yield (per cent)	Analysis	
				Required N (per cent)	Found N (per cent)
I	C_6H_5	114	73.9	—	—
II	2-HO-C_6H_4	134—135	84.6	7.65	7.9
III	2-Cl-C_6H_4	132—134	88.8	6.9	7.0
IV	3-Cl-C_6H_4	133—134	88.8	6.9	7.2
V	4-Cl-C_6H_4	136—137	93.0	6.9	7.2
VI	2, 4-Cl_2-C_6H_3	158—159	89.4	5.9	6.2
VII	3, 4-Cl_2-C_6H_3	143—144	95.4	5.9	6.15
VIII	2, 5-Cl_2-C_6H_3	147—148	95.3	5.9	6.2
IX	2, 4, 5-Cl_3-C_6H_2	153—154	98.7	5.2	5.4
X	2, 4, 6-Cl_3-C_6H_2	155—156	93.5	5.2	5.4
XI	2, 3, 4, 5, 6-Cl_5-C_6	165—166	95.6	4.2	4.2
XII	2-CH_3-C_6H_4	105.5—107	85.5	7.7	8.0
XIII	3-CH_3-C_6H_4	95—95.5	84.2	7.7	7.8
XIV	4-CH_3-C_6H_4	136.5—137.5	89.0	7.7	7.9
XV	4-Cl-2-CH_3-C_6H_3	139.5—140.5	90.9	6.5	6.65
XVI	4, 6-Cl_2-2-CH_3-C_6H_2	148—149	94.7	5.6	5.9
XVII	2-NO_2-C_6H_4	156.5—157	80.0	13.2	13.5
XVIII	3-NO_2-C_6H_4	143—144.5	91.2	13.2	13.15
XIX	4-NO_2-C_6H_4	156—157.5	86.3	13.2	13.4
XX	2, 4-Cl_2-5-NO_2-C_6H_2	145—146	70.1	10.0	10.15
XXI	$C_{10}H_7$-1	139—140.5	92.1	6.45	6.5
XXII	$C_{10}H_7$-2	162—163	93.2	6.45	6.5

Experiments on the fungistatic activity of the compounds have been carried out by R. Kowalik and E. Czerwińska (Mycological Laboratory, Institute of Dyes and Intermediates, Warsaw) using the phenol-test method. The results are presented in Table II.

The activity of the substances has been compared with known fungicides, such as "spergon" and *p*-chlor-*m*-cresol used for the protection of plants.

It is possible to draw some general conclusions on the relation between the activity of the compounds and their chemical structure:

(1) a marked influence is produced by substituents in benzene rings and their positions;

(2) complete lack of activity is shown by the compounds with one nitrogroup attached to the benzene ring;

(3) substitution with chlorine in *para* position leads to a compound with selective activity towards *Fusarium culmorum*. Substitution with

two chlorine atoms in positions 2,4-, 3,4- and 2,5- leads to the formation of compounds with strong fungicide activity. Among trichloro derivatives the compound 2, 4, 6- (XII) is much more active than its isomer 2, 4, 5;

(4) *p*-Methylphenoxyacethydroxamic acid (XIV) is more active than the other phenoxyacethydroxamic acids. This seems to indicate the

TABLE II

Fungicide activity of aryloxyacethydroxamic acid derivatives

No.	Concentration in per cent of the examined substance in the agar culture medium, completely inhibiting the growth of the fungi		
	Fusarium culmorum	*Alternaria solani*	*Rhizoctonia solani*
I	—	—	—
II	0.5	0.5	0.5
III	0.25	0.1	0.1
IV	0.1	0.05	0.1
V	0.05	0.25	0.5
VI	0.025	0.025	0.025
VII	0.05	0.025	0.025
VIII	0.05	0.05	0.025
IX	0.5	0.5	0.5
X	0.05	0.05	0.025
XI	0.5	0.5	0.5
XII	0.5	0.5	0.5
XIII	0.5	0.25	0.25
XIV	0.05	0.1	0.05
XV	0.005	0.5	0.05
XVI	0.5	0.5	0.5
XVII	1.0	1.0	1.0
XVIII	1.0	0.5	0.25
XIX	1.0	1.0	1.0
XX	0.05	0.05	0.05
XXI	0.05	0.05	0.05
XXII	0.5	0.5	0.25
Spergon *)	0.125	0.125	0.125
p-chloro--*m*-cresol	0.01	0.01	—

activating influence of *para* substituents, whether the substituent is of the chlorine or methyl group.

4-Chloro-2-methylphenoxyacethydroxamic acid (XV) is particularly active against *F. culmorum* and *Rhizoctonia solani*. Pentachloroderivative (XI) possesses no activity and, on the contrary, the 2, 4-dichloroderivative of 5-nitrophenoxyacethydroxamic acid (XX) is active;

(5) Among the naphthalene derivatives, 1-naphthoxyacethydroxamic acid (XXI) is strongly fungistatic and much more active than 2-naphtho-

*) The trade-name of 2, 3, 5, 6-tetrachloro-*p*-benzoquinone, used as seed dressing.

xyacethydroxamic acid (XXII). This is a striking example of a "reversed physiological activity" of 1- and 2-derivatives of naphthalene, as 2-naphthoxyacetic acid is a plant growth-promoting agent and 1-naphthoxyacetic acid is inactive.

To check partly this observation, 1-naphthylacethydroxamic acid (XXIII) (m. p. 164—165° with decomp.) was prepared and examined. It has been found to be inactive against examined fungi, although 1-naphthylacetic acid, its ester and amide are particularly active growth-promoting agents.

(6) A similar lack of fungicide activity shows α-phenoxyisobutyrhydroxamic acid (XXIV) (m. p. 132—133.5° with decomp.), although some derivatives of α-phenoxyisobutyric acid are definitely fungistatic.

(7) Finally, it has been found that the products (VI), (IX) and (XV) do not show any stimulating effect on the growth of examined fungi, when used at the concentration 5.10^{-5} %. It indicates that there is no relation between fungicide activity and growth-promoting or herbicide activity of the chloroderivatives of aryloxyacetic acids and the corresponding derivatives of aryloxyacethydroxamic acids respectively.

The authors are much indebted to R. Kowalik and E. Czerwińska for testing the fungicide activity of the examined compounds.

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GEOLOGY

Observations on the Sedimentation of the Babica Clays (Palaeocene) in the Middle Carpathians

by

S. BUKOWY

Presented by M. KSIĄŻKIEWICZ on July 11, 1956

The present paper concerns the sedimentary features of the Babica clays, and seeks to explain their origin.

Stratigraphic position

These beds were distinguished by B. Kropaczek [1] at the boundary of the Cretaceous and Palaeogene. In spite of their small thickness, the Babica beds, and associated conglomerates with exotics, comprise beds differing in lithology, usually forming large, flat lenses. In addition to sandstones and conglomerates, there are present loose sands and dark clays, i. e. the Babica clays proper. All these beds contain numerous pebbles of exotic rocks. The diversity of the composition of the Babica beds is in contrast with the monotonous character of the underlying Inoceramian beds and also with the surmounting Eocene variegated clays.

The Babica clays crop out in the southern flank of the Kąkolówka anticline and in the Ropczyce folds. In age, according to Kropaczek [1], they are Lower Eocene and Palaeocene; this view was confirmed by Rogala [3] and Bieda [5]. Beds resembling in composition the Babica clays occur also in the uppermost part of the Inoceramian beds, and in the lowest portion of the Eocene.

Sedimentary features of underlying beds

The Inoceramian beds consist of thin-bedded and fine-grained sandstones, and calcareous mudstones with rare glauconite alternating with grey-green shales and marls. There are a few intercalations of medium-grained, graded sandstones and sets of alternating shales and sandy marls a few metres thick. Both sandstones and marls reveal fine lamination often contorted by sliding. Two types of laminated sandstones may be distinguished, one with distinctly marked gradation, and another

without any gradation. In the first type, the grain is more coarse and some grading is often visible in the lower part of the laminated bed. Contortions are rare in this type of sandstones and limited only to the upper part of beds. Current hieroglyphs (flow marks) are usually present, directed towards the south-east. This direction is constant over a fairly large area and does not undergo changes in the vertical profile.

The un-gradational type of lamination is visible in the very fine-grained sandstones, mudstones and marls. Laminae often wedge out, truncated by the overlying laminae. Contortions are frequent and developed in the middle or lower part of beds. Contortion folds are directed towards the south, a fact which implies that the direction of flowing did not coincide with the direction of sliding. It may be that the sea bottom had sloped gently towards the south, and that currents transporting sand and mud had been flowing to the south-east, while the deposits laid down had, under influence of gravity, been sliding with the slope to the south.

The fauna, consisting of *Inoceramus* shells and agglutinated foraminifera, occurs only in shales. The microfauna has the features of a deep water fauna, from which, as also from the prevalence of lamination, fine grain and continuity of particular sandstone beds, it may be inferred that the deposit was laid down at a distance from the coast.

It the uppermost part of the Inoceramian beds, the monotonous type of sedimentation undergoes considerable changes; there is an increase in the rate of sedimentation, marked by graded coarse-grained sandstones, while conglomerates with exotic rocks also appear.

Sedimentary features of the Babica beds

The Inoceramian beds pass upward into a series comprising graded conglomerates and sandstones, together with current-bedded sands. Marls and clays occur only subordinately, and the calcareous cement is much less frequent than in the underlying beds.

Conglomerates contain pebbles of quartz, acid volcanic rocks, and not very abundant coal fragments. Quartz is well rounded, while pebbles of limestones are poorly rounded and resemble dreikanters in shape. The surface of limestone pebbles is considerably pitted. Fragments of porphyries are only slightly rounded, but distinctly weathered. Pebbles of prolate shape are oriented, demonstrating an imbrication; it may be presumed that they were deposited under a current flowing from north-west toward south-east as has been measured already in this area by Książkiewicz [10]. Conglomerates of the Babica clays contain broken shells of pelecypods (some of them thick-shelled), gastropods, bryozoans and *Lithothamnia*. On the other hand, shales and clays underlying and covering conglomerates have always an agglutinated microfauna of a deep-water character. This may suggest that the conglomerates are, in spite

of the shallow-water character of their fauna, a deep-water deposit, and that their fauna is redeposited together with the detrital material from a shallow-water environment. Similar phenomena have been described from other parts of the Carpathians by Książkiewicz [9], [10].

The conglomerates described above are covered by the Babica clays occuring in a lens, 12 m. thick. As a matter of fact, they consist of pelitic quartz and contain very little argillaceous matter. The unconsolidated material contains numerous pebbles of various dimensions (up to 2.5 m. in diameter) of exotic rocks, and also fragments of the Flysch rocks, sandstones, conglomerates and shales, torn out from the base of the Babica clays. The fauna occurs in the clays, but is not uniformly distributed. On the whole, the fauna is poorly preserved. It comprises gasteropods, pelecypods, bryozoans, corals and *Lithothamnia*. Microfauna has the character of a mixed assemblage: beside benthonic forms indicating a warm water environment, agglutinated foraminifera occur in considerable numbers. Some foraminifera are well, others poorly preserved.

Pieces of coal, dolomites and limestones of the Devonian and Carboniferous, limestones of the Jurassic, and slates are abundantly represented among the pebbles occurring in the Babica clays. Although pebbles are well rounded, some of them are strongly weathered.

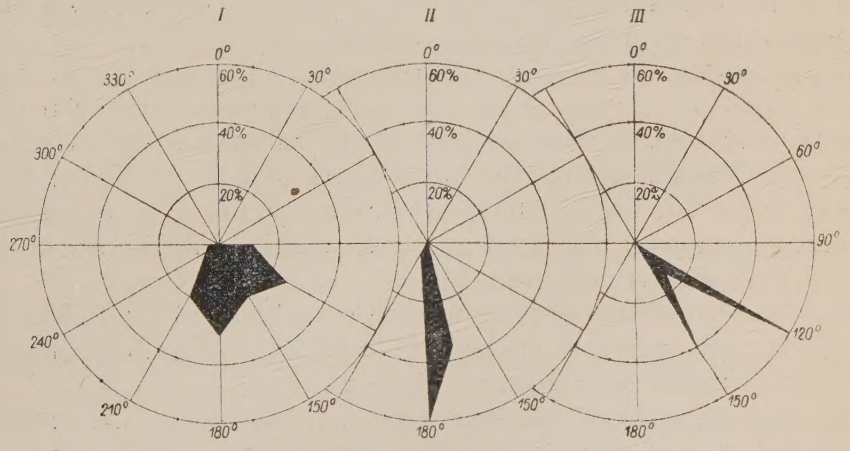

Fig. 1. Direction of flow: I. In the Eocene; II. In the Babica clays; III. In the Inoceramian beds.

Pebbles are more numerous in the lower part of the lens while in the topmost parts there are none. In this way, the deposit exhibits some grading; this is emphasised by the appearance of lamination in the upper part of the lens. Pebbles have a fairly constant orientation of their longer axes, which dip usually 7 to 14 degrees towards the south. Pebbles lying at the very bottom of the lens, are pressed into the underlying clay or sandstone, but have the same orientation as pebbles lying inside the lens. From the orientation of pebbles, one may assume that the material

was transported from the north; the same direction is indicated by the presence of furrows and grooves visible on the upper surface of underlying beds.

Orientation of pebbles, as described above, is, according to A. Cailleux [4], characteristic for the sub-littoral zone, but the general character of the deposit, as described above, suggests that it could be deposited by slumping and mixing of shallow water sediments loaded with pebbles and containing a sub-littoral fauna with sediments from the deeper sea containing agglutinated microfauna. This type of translocation may correspond to an intermediate form between a submarine slump as described by Archangelsky [2] and a turbidity current as envisaged by Kuenen and Migliorini [6]: it could also be a feebly diluted submarine mud-flow. Poorly marked grading indicates that the material was not thoroughly mixed with water; only the top part exhibiting lamination was deposited from that part of the current where dispersion was greater. On the other hand, the mud-flow must have had a considerable erosive power since it grooved the bottom and tore from it large fragments. Therefore it lies discordantly on its base, reposing either on a conglomerate or on the sandstones or shales underlying the conglomerate. The velocity of the current must have been considerable, although Ph. H. Kuenen and H. W. Menard [8] experimentally obtained products intermediate between those of the mud-flows and turbidity currents at velocities much lower than those of proper turbidity currents.

The orientation of pebbles in the deposit is the opposite to that of pebbles occurring in the underlying conglomerates. But when in the latter deposit pebbles were dragged along the bottom by the current, in the mud-flow deposit the motion of particles was caused not by the drag by water but by gravitative slumping. In this type of transport, the more loaded lower part may, as found experimentally by Ph. H. Kuenen [7], have greater velocities.

The direction of transport during the depositions of the Babica clays changed towards the south in comparison with the direction of transport in the Inoceramian beds (towards the south-east).

The sedimentation of the Babica clays is marked by the change in the mechanism of deposition and, to a certain extent, also by changes in directions of transport. This change is due, probably, not to shallowing of the sea but to an increase in inclination of the sea bottom. It may be presumed that this was caused by the tectonic movements connected with the Laramian orogenic stage.

Sedimentary features of overlying beds

The beds overlying the Babica clays display other features; at first, diagonal bedding is prevalent in sandstones; later, graded bedding both in sandstones and conglomerates. Grading is usually multiple and pensymmetric [10].

These beds pass upwards into medium- and fine-grained sandstones, with lamination which is always gradational, with finer grades and thinner laminae upwards. There are no hieroglyphs on the smooth surfaces of sandstones, and generally no shales between the sandstones. Conglomerates are composed mainly of crystalline rocks (quartz, gneisses, slates) while Palaeozoic limestones are rare. Pebbles of the Inoceramian sandstones are present.

It is possible that these beds were deposited by fairly swift turbidity currents which swept the bottom of clay and deposited sand and gravel directly on sandy layers.

Lack of flow marks makes it difficult to determine the direction of currents, and the orientation of pebbles in conglomerates is somewhat chaotic. In many instances, however, it was found possible to ascertain that the current bedding was directed southward, which seems to indicate that no change in direction of transport occurred.

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